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Batch Microreactor Studies of Lignin Depolymerization by Bases. 2. Aqueous Solvents

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Abstract

Biomass feedstocks contain roughly 15-30% lignin, a substance that can not be converted to fermentable sugars. Hence, most schemes for producing biofuels assume that the lignin coproduct will be utilized as boiler fuel. Yet, the chemical structure of lignin suggests that it will make an excellent high value fuel additive, if it can be broken down into smaller compounds. From Fiscal year 1997 through Fiscal year 2001, Sandia National Laboratories participated in a cooperative effort with the National Renewable Energy Laboratory and the University of Utah to develop and scale a base catalyzed depolymerization (BCD) process for lignin conversion. SNL's primary role in the effort was to perform kinetic studies, examine the reaction chemistry, and to develop alternate BCD catalyst systems. This report summarizes the work performed at Sandia during Fiscal Year 1999 through Fiscal Year 2001 with aqueous systems. Work with alcohol based systems is summarized in part 1 of this report.

Our study of lignin depolymerization by aqueous NaOH showed that the primary factor governing the extent of lignin conversion is the NaOH:lignin ratio. NaOH concentration is at best a secondary issue. The maximum lignin conversion is achieved at NaOH:lignin mole ratios of 1.5 - 2. This is consistent with acidic compounds in the depolymerized lignin neutralizing the base catalyst. The addition of CaO to NaOH improves the reaction kinetics, but not the degree of lignin conversion. The combination of Na₂CO₃ and CaO offers a cost saving alternative to NaOH that performs identically to NaOH on a per Na basis. A process where CaO is regenerated from CaCO₃ could offer further advantages, as could recovering the Na as Na₂CO₃ or NaHCO₃ by neutralization of the product solution with CO₂. Model compound studies show that two types of reactions involving methoxy substituents on the aromatic ring occur: methyl group migration between phenolic groups (making and breaking ether bonds) and the loss of methyl/methoxy groups from the aromatic ring (destruction of ether linkages). The migration reactions are significantly faster than the demethylation reactions, but ultimately demethylation processes predominates.

1. Introduction

Lignins are complex polymers found in nature where they provide strength to vascular plants. Chemically, they are a polymer of phenylpropane-based monomers joined by ether and carbon-to-carbon linkages. In native (unprocessed) lignins, generally two thirds or more of the total linkages are ether bonds, while the remaining are carbon-carbon bonds [1]. Several common linkages between the phenylpropane monomers are shown in Figure 1 below.

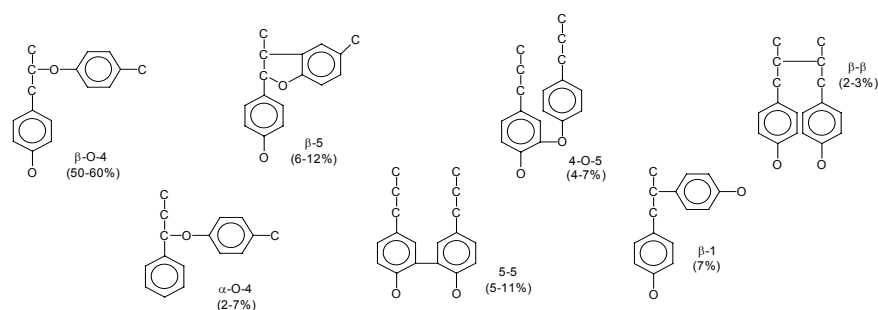


Figure 1. Chemical bonds commonly found in lignin – the monomer units have been simplified for clarity.

All lignocellulosic biomass contains significant quantities of lignin (roughly 15-30%). Unlike cellulose and hemicellulose, the other principal constituents of biomass, lignin can not be converted to fermentable sugars. Thus, any fermentation-based ethanol production process (from biomass) will produce a large quantity of lignin by-product. Most of the lignin entering a biomass-to-ethanol process will be present in the solid residue remaining after the dilute acid pretreatment and simultaneous saccharification and fermentation (SSF) steps. This high molecular weight lignin is soluble in aqueous basic solutions, and can be readily recovered from the protein, unconverted carbohydrate, and other non-lignin materials present in the residue by solubilization.

Capturing the value of the lignin residue will significantly enhance the economic competitiveness of biomass-to-ethanol conversion. The simplest approach to lignin utilization is to burn the residue for process heat, as is currently done in the pulp and paper industry (this also helps recover valuable pulping chemicals for recycle). However, given the molecular structure of lignin, it is potentially more productive to convert the lignin into valuable high-octane fuel additives (gasoline blending agents) such as aromatic hydrocarbons and/or ethers. From Fiscal Year 1997 through Fiscal Year 2001, Sandia National Laboratories was a participant in a cooperative effort with the National Renewable Energy Laboratory (NREL) and the University of Utah to develop and scale-up a process for this conversion.

The process in question, originally proposed and researched by Shabtai and coworkers [2], is a two stage process related to processes developed for coal liquefaction [3]. In the first step, termed base-catalyzed depolymerization (BCD), ether linkages are broken by heating the lignin to moderate temperatures (ca. 300 °C) in the presence of base, resulting

in smaller and lower molecular weight lignin products. Because smaller molecular weight compounds tend to have greater solubility, the extent of depolymerization can be characterized by the amount of water and ether insoluble material remaining after the reaction. The second stage involves hydroprocessing the depolymerized lignin intermediate.

In earlier studies, supercritical methanol or ethanol was used as the reaction medium and KOH was the preferred base for the BCD step. These choices were based on the successful application of these materials to the depolymerization of low-rank coals [3-12]. Sandia's contribution to these studies is presented elsewhere [13,14,15]. Briefly, batch microreactor studies demonstrated that the conversion of lignin to ether solubles by KOH in methanol or ethanol is rapid at 290 °C, reaching the maximum value (only 7% ether insoluble material remaining) within 10-15 minutes. Model compound studies confirmed that dominant depolymerization route is the solvolysis of ether linkages. Strong bases (KOH, NaOH, CsOH) were shown to convert more of the lignin to ether soluble material than weaker bases (LiOH, Ca(OH)₂, and Na₂CO₃). An excess of base relative to lignin monomer units is required for maximum conversion. However, a synergistic interaction between NaOH and Ca(OH)₂ allows reasonable conversions of lignin to be achieved with small amounts of NaOH by coupling it with Ca(OH)₂. Ethanol and methanol are converted to acetic and formic acid respectively under the reaction conditions with an activation energy of approximately 50 kcal/mol. This results in a loss of solvent, but more importantly neutralizes the base catalyst, halting forward progress of the reaction, and accounting for the excess base requirement.

In late Fiscal Year 1998, the focus of the program shifted away from alcohol solvents and KOH, in favor of aqueous NaOH. This was a direct result of economic analyses of the lignin conversion process performed by NREL [16]. Among other reasons for the change, methanol and ethanol, valuable materials in themselves, tend to be incorporated into the lignin during the BCD step without adding value to the products. The alcohols are also consumed by other side reactions to form organic acids and longer chain alcohols. NaOH is simply less expensive and comparable in performance to KOH. In this report we summarize work performed at Sandia National Laboratories to develop and optimize an aqueous BCD process.

2. Experimental

It was our experience that the experiment to experiment variability is greater when using water as a reaction solvent than when alcohols are used as solvents. To minimize the effect this might have on the outcome and interpretation of our experiments, we have tried to run complete sets of experiments all at once, with all the experiments performed by a single person. When possible, we have avoided including data taken from different sets of experiments and/or data from experiments performed by different people in a single chart or comparison.

2.1 Reaction Testing:

2.1.1 Lignin Sources: The technical lignin samples used in this study were obtained from the manufacturers by the National Renewable Energy Laboratory and supplied to Sandia

National Laboratories where they were used in the as-received condition. The Alcell lignin sample from Repap Technologies Inc. (Valley Forge, PA) was derived from mixed hardwoods by an ethanol organosolv pulping method. Analysis of this lignin [17] shows that it is indistinguishable from lignins used in the two-dimensional round robin lignin analysis conducted in 1991 for the International Energy Agency, Bioenergy Agreement, Biomass Conversion Annex VII.

2.1.2 Batch Microreactors: Reaction tests were carried out in batch microreactors consisting of capped $\frac{3}{4}$ " Inconel 600 Swagelok unions. Stainless steel fittings used in the initial studies with aqueous systems all rapidly developed leaks, probably due to stress corrosion cracking. Modifications in the procedure were made as necessary, and are described in the Results and Discussion section below. The standard experiment was performed as follows: First, the desired amount of Alcell lignin was weighed into the reactor. Solid bases were directly weighed into the reactor as well. The desired amount of water (or NaOH solution) was then added to the reactor, and the reactor was securely sealed. Typically, the amount of water added to the reactor was adjusted to give near 100% saturated liquid at the planned reaction condition, and the amounts of base and lignin were adjusted accordingly to maintain the desired ratios (typically 10:1 base solution:lignin by weight). The sealed reactors were then rapidly heated in a fluidized sand bath to the desired reaction temperature (290 – 330 °C). A wrist action shaker was used to provide some degree of mixing while the reactors were in the heated sand baths. After the desired reaction time had elapsed, the reactors were removed from the sand bath and quenched in water.

After the reactors were cooled, they were carefully opened, relieving the pressure resulting from the formation of gaseous products. If pressure was not released upon opening, the contents were discarded and the experiment was repeated. The liquid and solid products of the reaction were rinsed from the vessel with deionized water and acidified to a pH of 2 (verified by pH paper) with concentrated HCl converting the solid base (e.g. CaO) to a soluble product and causing an organic precipitate to form. The acidified products were covered and refrigerated overnight to allow the precipitate to grow and settle. The solid products were then recovered with a preweighed Whatman 541 filter. The solids were rinsed/extracted with deionized water followed by diethyl ether. The filter paper and remaining solids were allowed to air dry, and were then transferred to a 45 °C drying oven. After drying overnight, the filter papers and remaining solids were removed from the oven, allowed to air equilibrate for at least one hour and weighed. The results are expressed as the mass of unconverted lignin as a percentage of the original mass. All experiments were repeated from two to four times and the data presented here represent averages of the duplicates. Standard conditions for the reaction were 290 °C, one hour reaction time, 0.59 g Repap Alcell lignin, 10:1 solvent:lignin ratio, 1% NaOH solution (0.0015 moles OH⁻ in the reactor), and 0.0091 OH⁻ equivalents of solid base in an 8 ml reactor.

2.1.3 Comments on Heatup and Stirring in Batch Microreactors: At various times in this program, concerns were raised regarding the use of the microreactors for this work, and the applicability of the results to other systems. The microreactors have several

advantages, including rapid heat up and cooling (thereby facilitating kinetic studies), but have limited mixing capabilities. In contrast, many of the experiments performed at the University of Utah were conducted with larger autoclaves that are very well-mixed, but are slow in reaching reaction temperature. Hence, we conducted several experiments designed to discover if the differences between the reactors could lead to discrepancies in results.

The first series of experiments involved slowly ramping the temperature of the sand baths from room temperature to 290 °C over a period of one hour. Duplicate reactors containing standard amounts of 1% NaOH, lignin, and CaO were placed in the sand bath during this period. In one experiment, the reactors were removed immediately after the bath reached 290 °C and were then quenched. In a second experiment, the reactors were held in the bath at 290 °C for 15 minutes following the ramp, and were then removed and quenched. A third experiment was identical to the second with the exception that a zirconia bead was added to the reactor in an attempt to enhance the mixing, similar to the bead in a can of spray paint. The results of these experiments are compared to a control (15 minute reaction at 290 °C with standard heatup and mixing) in Figure 2. It is clear from the figure that the slow temperature ramp had no positive effect on conversion. Thus, we conclude that different heatup profiles do not lead to pronounced differences in conversion, at least at 290 °C where the reaction is still relatively slow. However, the enhanced mixing may have had a small positive effect.

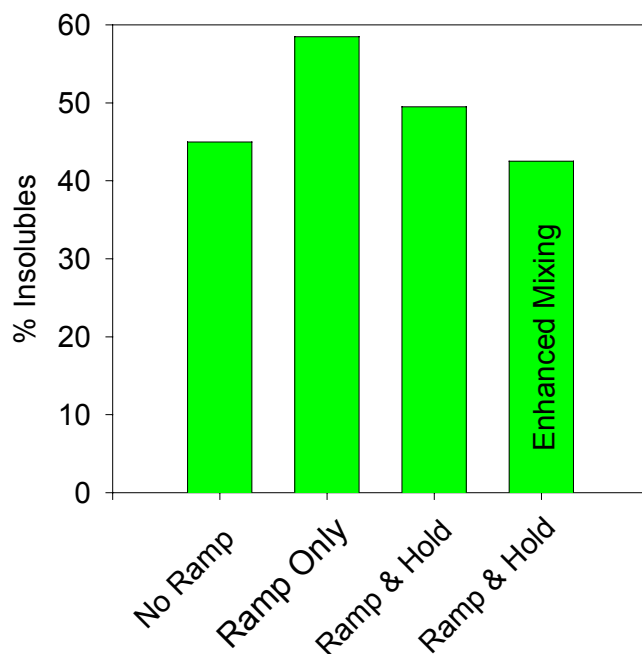


Figure 2. Slowly heating the reactor to 290 °C gives no improvement in conversion.

Additional experiments were carried out to further evaluate the effect of mixing enhancements. The reactions were carried at 290 °C for one hour with standard ratios of 1% NaOH, CaO, and lignin. In one set of reactions, a zirconia ball was included in the reactor contents to improve agitation. In a second set of reactions, the amount of material

added to the reactor was halved so that a significant vapor space would be present, providing the liquid with room to “slosh” and mix in the reactor. Ratios of NaOH, lignin and CaO were kept constant. In the third set of reactions, the amount of material added to the reactors was halved and a zirconia ball was also added. The results are compared to a control experiment in Figure 3. The steps taken to improve mixing clearly only offer a slight improvement, as the insolubles still fall in the 25-35% range. Unfortunately, even with enhancements, our mixing falls short of that provided in a well designed autoclave. Therefore, from these experiments, we can not entirely rule out differences in mixing as a factor that must be considered when comparing results from different systems, or designing a larger scale system. However, we note that, in general, our results are consistent with those obtained at NREL and at Utah, provided that they are appropriately compared (e.g. at equivalent Na:lignin mole ratios, see below). Given the absence of an effect of the temperature ramp on the results, and the small effect of mixing, all other experiments reported herein were conducted under the conditions of rapid heat-up with no mixing enhancements, unless otherwise stated.

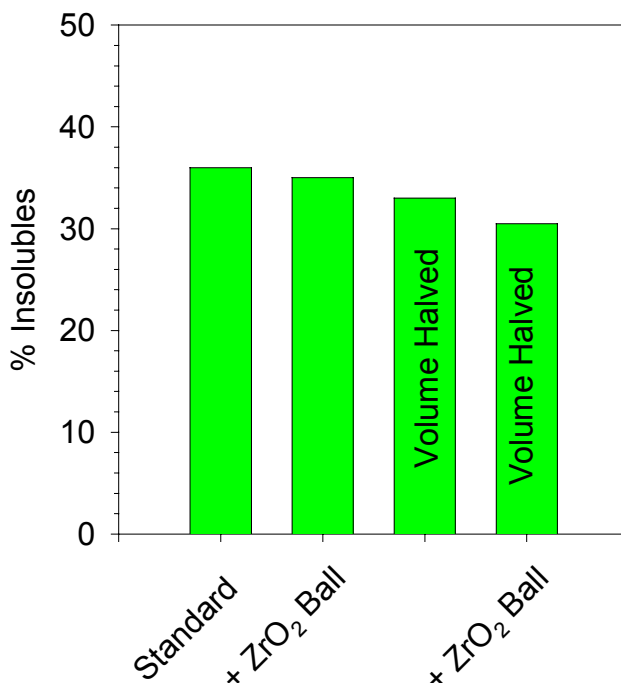


Figure 3. Improvements to enhance mixing result in only a slight increase in conversion.

2.2 Catalyst Preparation:

The NaOH, Ca(OH)₂, and Mg(OH)₂ used in this study were obtained from Fisher Scientific. Solutions of NaOH were prepared with DI water and weighed into the reactors as such. Ca(OH)₂ and Mg(OH)₂ were added directly to the reactors as the as-received powders. CaO and MgO were prepared by calcining the as-received Ca(OH)₂ and Mg(OH)₂ powders for three hours at temperatures ranging from 400 to 700 °C. The calcined powders were removed from the furnace, cooled, and then immediately weighed into the reactors. Samples of CaO and MgO prepared in this way were saved to determine the effect of air exposure on performance. CaO, Na₂CO₃, and MgO were also

obtained from Fisher Scientific and used in the as-received condition. MgO obtained from Premier Services Corp. (Magox) was used in the as-received condition and after a three hour air calcination at 500 °C.

2.3 Lignin Solubility:

The approximate room temperature solubility of Repap Alcell lignin was determined for solutions containing 1, 2, and 3% NaOH (w/w). For each determination, several vials were prepared, each containing 10 gram samples of the particular NaOH solution. Lignin was then added to each vial in increasing amounts. The contents of the vials were then agitated using a wrist-action shaker for about 15 minutes. The contents of each vial were then filtered through a Whatman 541 filter. After the filter papers were dry, they were examined for the presence of sediment (undissolved lignin). The approximate solubility point was then determined as the highest lignin concentration that fully dissolved, leaving no residue on the filter paper. The estimate was then refined by taking additional data near the previously determined solubility using new samples separated by small weight increments.

2.4 Calculation of Thermodynamic Equilibrium Constants:

Thermodynamic equilibrium constants were calculated using the software HSC Chemistry Version 2.0.

2.5 Model Compound Studies:

2.5.1 Reaction of Syringol in Aqueous NaOH: These reactions were carried out by mixing 0.1g (6.48×10^{-4} mol) of syringol (2,6-dimethoxyphenol) in 5g 1% NaOH (0.00125 mol) giving a Na:Syringol ratio of 1.9:1. The reaction mixture was sealed in 3/4" Swagelok bulkhead unions serving as microreactors. The reactors were then heated in a fluidized sand bath to 290 °C, for 0, 10, 30, 45, 60, and 90 minute periods while being agitated with a wrist action shaker. At least two, and often four, duplicate reactions were carried out for each time period. Following reaction, the reactors were rapidly quenched with water, and the contents were acidified with HCl to a pH of 5. This pH was chosen on the basis of a series of trials that showed that this pH gave the highest sensitivity when using a DB-5 GC column. After neutralization, the contents were mixed with 3.5 g of acetone, to prevent the precipitation of solids. Analysis was conducted with an HP 5890 gas chromatograph using a narrowbore 30 meter DB-5 column and FID detector. For quantification, each sample was analyzed a minimum of five times and the results were averaged. Product identification was carried out by using the same column in an HP 5890 gas chromatograph with a series 5972 mass selective detector. Standards of each compound were purchased to ensure correct identification and quantification. The standards were dissolved in aqueous NaOH, neutralized with HCl to a pH of 5, and diluted in acetone, similar to the actual reaction products. Standard solutions containing only one standard compound and with several compounds were prepared and analyzed at different concentrations to test for matrix effects. Matrix effects were minimal and the sensitivity of the FID to a given compound scaled almost linearly with the number of carbon atoms, as expected.

2.5.2 Reaction of Syringol and Phenol in Aqueous NaOH: These experiments were performed using 2% syringol and 2.5% phenol in 1% NaOH. The reactions were carried out by mixing 0.1g of syringol (6.48×10^{-4} mol) and 0.125 g of phenol (1.33×10^{-3} mol) in 5g 1% NaOH (0.00125 mol) giving a phenol:syringol molar ratio of about 2:1 and a Na:organic molar ratio of about 2:3. Otherwise the reactions were carried out as for the syringol study.

2.5.3 Reaction of Anisole in Aqueous NaOH: Initial reactions were conducted at 290 °C for 1 hour with anisole (methoxybenzene) NaOH ratios of 1:2, 1:1, and 2:1. Additional time-dependent studies utilized 0.5g of anisole (0.0925 mol) in 3.7g 5% NaOH (0.0925 mol). Samples were neutralized and analyzed as before.

2.5.4 Reaction of Phenol and Methanol in Aqueous NaOH: Equal molar amounts of phenol, methanol, and NaOH were reacted at 290 °C for 60 min and analyzed as before.

2.5.5 Reaction of Methanol in Aqueous NaOH: The tests were performed by mixing methanol into 1% NaOH at a specific ratio and reacting for 60 min at 290 °C. The samples were then titrated using a Mettler autotitrator with 0.1N HCl to determine the base concentration.

3. Results and Discussion

3.1 Baseline Studies with Aqueous NaOH:

Initially, a number of screening experiments were carried out with 10% (w/w) aqueous solutions of NaOH as the catalyst to provide a tie to the previous studies using alcohol solutions. These studies also provide a useful baseline for studies of alternate base systems. The results of these initial tests are shown in Figure 4. Clearly, as with the alcoholic NaOH system [13], high conversions of lignin to water and ether solubles are possible in the aqueous NaOH system. With 10% NaOH, and equal weights of NaOH and lignin in the reactor (a stoichiometric excess of base), only 8% insoluble material remained after reaction at 330 °C for one hour.

As shown in Figure 5, screening experiments were also performed to determine if the lignin conversion varied with NaOH concentration. The results were unexpected. Given that there were no alcohols present in the system to be converted to acids and thereby neutralize the base [13], and the long reaction time, it seemed likely that small quantities of base would give conversions nearly identical to the higher concentrations. In fact, the data is very similar to that obtained for the NaOH ethanol system in that the conversion appears to result more from stoichiometric rather than catalytic processes. There are at least two plausible rationalizations for this behavior. One possibility is that kinetic effects give a false impression (e.g. the reaction time is too short, or there are competing noncatalytic retrograde reactions). The second possibility is that there are indeed stoichiometric effects (e.g. acidic products from the lignin interacting with the base). It will be shown below that, although the reaction is slower in water than methanol or ethanol, the observed behavior results from stoichiometric interactions.

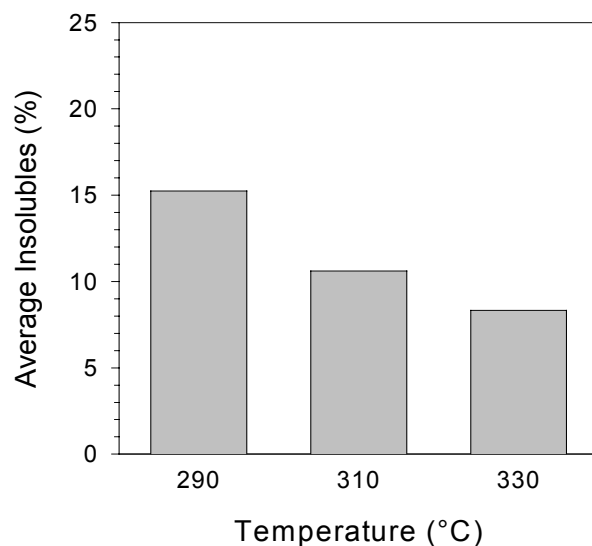


Figure 4. Effect of temperature on lignin conversion. Reactions were carried out at the given temperature for 1 hour with 10% NaOH solutions and a 1:1 NaOH to lignin weight ratio. The total amount of water in the reactor was adjusted to give nearly 100% saturated liquid at the reaction temperature.

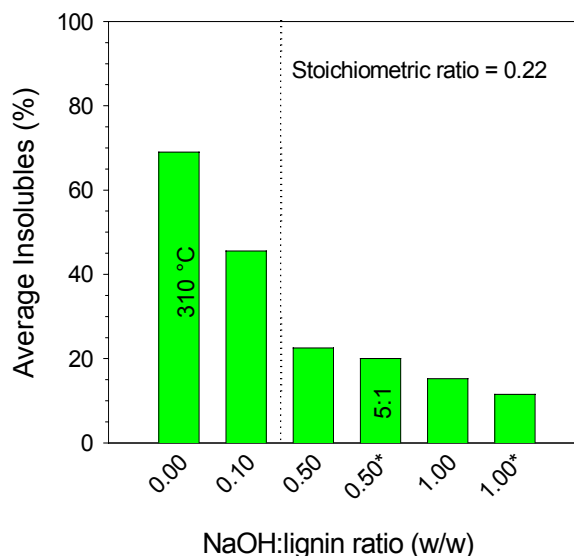


Figure 5. Effect of base concentration on lignin conversion. Reactions were carried out at 290 °C for 1 hour except the zero base control (310 °C). The heated reactors contained nearly 100% saturated liquid, except the cases marked * which used ½ the water giving 95% saturated liquid. The solvent:lignin ratio was 10:1 except for the case marked 5:1.

3.2 Baseline Kinetic Studies with Aqueous NaOH:

In section 3.1, data is presented that shows lignin conversion is strongly correlated with the NaOH concentration. One possible reason for this is slow reaction kinetics in the aqueous system. Kinetic data for a 10% NaOH solution (Figure 6) shows that the reaction is fairly rapid. The insolubles reach a minimum value (15%) within the first 25 minutes of reaction. This compares reasonably well with the data collected for 10%

KOH in methanol where the insolubles reached a minimum of about 15% within the first 15 minutes of reaction [13]. However, the data collected for the 1% NaOH solution shows that even after two hours of reaction time, the level of insolubles (34%) does not approach the low level achieved for the 10% solution, and it is also still significantly higher than the 23% insolubles remaining after 1 hour when 5% NaOH was used (Figure 5). Thus, slow kinetics seems to provide at least a partial explanation for the limit to conversion in 1% NaOH after 1 hour. Yet, since the insolubles only decreased from 46% after one hour to 34% after 2 hours, it appears that an additional effect such as base neutralization by reaction products may also be operative.

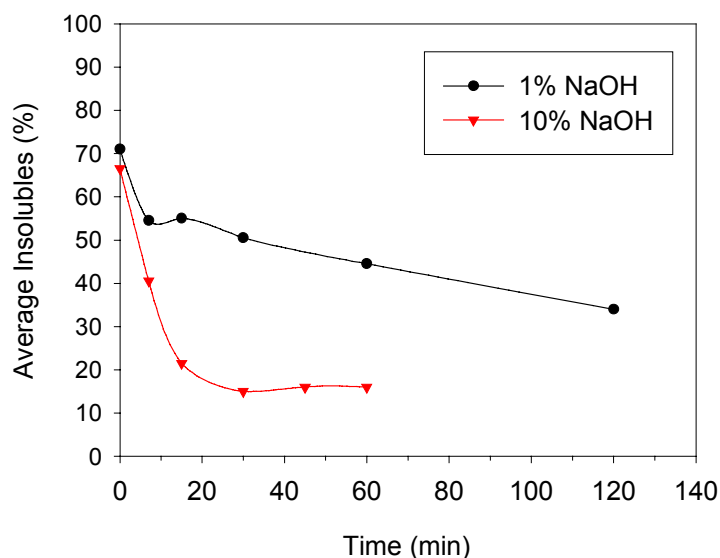


Figure 6. Effect of NaOH concentration on rate of Repap lignin depolymerization in aqueous system. Reactions carried out at standard conditions: 100% saturated water and 10:1 solvent:lignin (w/w).

3.3 Baseline Studies of Ca and Mg Oxides and Hydroxides as Catalysts:

In our study of base driven lignin depolymerization in alcohol solvents [13], we developed an alternate catalyst system that combined NaOH with $\text{Ca}(\text{OH})_2$ to achieve high lignin conversions at potentially lower costs. It is thought that the NaOH in this system acts as a catalyst for ether bond cleavage, while the $\text{Ca}(\text{OH})_2$ functions as a sacrificial base to neutralize acidic products that are formed during the reaction. Given the results presented in section 3.2 suggesting that catalyst deactivation (base neutralization) might be a problem, it seemed reasonable to examine whether a similar base combination might function in an aqueous environment. The systems are not entirely analogous, however, since the alcohol solvents react to form the relatively strong formic and acetic acids, while the acidic products in the aqueous system must originate from the lignin and would be anticipated to be relatively weak acids such as phenols. A second motivation for examining calcium and magnesium bases is that they are solids with relatively low solubility, raising the possibility that they could be easily separated and recovered for reuse.

The initial screening studies were carried out with NaOH, Ca(OH)_2 , and Mg(OH)_2 obtained from Fisher scientific, and with CaO and MgO prepared by calcining the same Ca(OH)_2 and Mg(OH)_2 powders for three hours at 500 °C. This method and temperature were chosen since numerous researchers have concluded that the highest basicity and activity are achieved when CaO is prepared from Ca(OH)_2 in this manner [18]. A temperature of 600 °C is reported to be optimum for the preparation of MgO [19]. The calcination of CaO or MgO activates the oxides by removing H_2O , CO_2 , and O_2 . However, since the materials were ultimately placed back in an aqueous environment, the main chemical effect of the calcination should be the destruction of carbonates. The calcined powders were removed from the furnace, cooled, and then immediately weighed into the reactors.

The standard conditions for the baseline reactions were 290 °C, 1 hour reaction time, a reactor loading giving nearly 100% saturated liquid water at the reaction temperature, and a 10:1 water:lignin ratio (~ 0.6 g lignin). The total amount of base (OH^- equivalents, i.e. Ca(OH)_2 , CaO, Mg(OH)_2 and MgO each give 2 OH^- equivalents/mol) added to the reactor in each case was 0.0106 mols. This is equivalent to about a 7% loading of NaOH. When NaOH was used in conjunction with the other bases, it was used at the 1% (w/w) concentration (0.0015 moles of NaOH) leaving 0.0091 moles for the calcium or magnesium base. These loadings were chosen for relative ease of comparison to the 1% NaOH data, and the data in Part 1 of this report [13].

The results for the calcium bases are shown in Figure 7 and the results for the magnesium bases are shown in Figure 8. As for the alcohol system, the results for the calcium and magnesium bases alone are disappointing. The best of these cases was for CaO where 49% of the original lignin mass was recovered as insoluble material. This is marginally better than the 55% with Ca(OH)_2 , but worse than 1% NaOH (46%). The magnesium bases performed very poorly by themselves. Mg(OH)_2 gave a solid material that could not be effectively recovered from the reactor. MgO resulted in 63% recovered solids. For comparison, Figure 5 shows that with no base at all only 69% of the material was insoluble after treatment at 310 °C.

The results with combinations of NaOH and magnesium and calcium bases were more promising. Combining 1% NaOH with CaO resulted in only 30% insoluble material and the combination with Ca(OH)_2 resulted in only 36% insolubles. Similarly the combination of NaOH with MgO only yielded 32% insoluble material. The combination of NaOH and Mg(OH)_2 was similar to NaOH alone. The synergies observed for NaOH combined with CaO, Ca(OH)_2 , and MgO are similar to that we observed for NaOH and Ca(OH)_2 in ethanol [13].

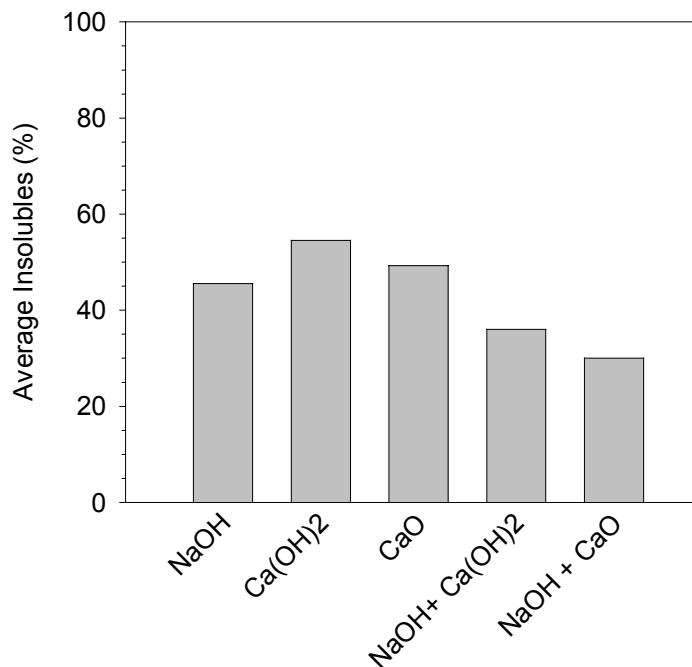


Figure 7. Lignin conversion (shown as insolubles remaining) in the presence of calcium bases (0.0106 OH⁻ equivalents) and calcium bases (0.0091 OH⁻ equiv.) combined with NaOH (0.0015 OH⁻ equiv.). Data for 1% NaOH (0.0015 OH⁻ equiv.) is shown for comparison.

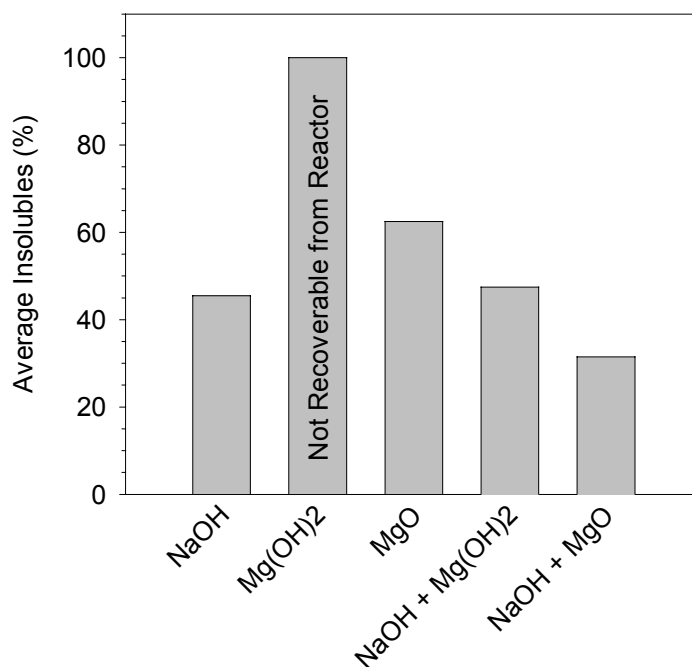


Figure 8. Lignin conversion (shown as insolubles remaining) in the presence of magnesium bases (0.0106 OH⁻ equivalents) and magnesium bases (0.0091 OH⁻ equiv.) combined with NaOH (0.0015 OH⁻ equiv.). Data for 1% NaOH (0.0015 OH⁻ equiv.) is shown for comparison. Data for Mg(OH)₂ is shown as 100% because material formed a solid material that was not recoverable from the reactor.

3.4 Detailed Studies of Ca and Mg Oxides and Hydroxides as Catalysts:

The initial success of combining NaOH with CaO, Ca(OH)₂, and MgO led to a series of further studies aimed at understanding and optimizing the system. The results of these studies are presented below.

3.4.1 Effect of CaO and MgO sources: A number of experiments were carried out with aqueous NaOH in combination with CaO and MgO from various sources. As before, NaOH, Ca(OH)₂, and Mg(OH)₂ were obtained from Fisher Scientific. CaO and MgO were prepared by calcining the Ca(OH)₂ and Mg(OH)₂ powders for three hours at 500°C. CaO was also obtained from Fisher Scientific and used in the as-received condition. MgO was also obtained from Fisher Scientific and from Premier Services Corp. (Magox) and used in the as-received condition. Magox was also used after a three hour calcination at 500 °C.

As before, the reactions were carried out at standard conditions of 290 °C, 1 hour reaction time, a reactor loading giving nearly 100% saturated liquid water at the reaction temperature, and a 10:1 water:lignin ratio (~ 0.6 g lignin). The total amount of base (OH⁻ equivalents, i.e. Ca(OH)₂, CaO, Mg(OH)₂ and MgO each give 2 OH⁻ equivalents/mol) added to the reactor in each case was 0.0106 mols. This is equivalent to about a 7% loading of NaOH. When NaOH was used in conjunction with the other bases, it was used at the 1% (w/w) concentration (0.0015 moles of NaOH) leaving 0.0091 moles for the calcium or magnesium base. For comparison, there were approximately 0.0033 moles of lignin monomer units in the reactor (assuming a molecular weight of 180 g/mol for the monomer). Hence there was about a 2:1 ratio of lignin monomers to Na atoms, but more than a 3:1 ratio of OH⁻ equivalents to lignin monomers. The results are shown in Figures 9 and 10.

As expected, Figures 9 and 10 show that there are significant differences between different calcium and magnesium oxides. An unexpected result was that the combination of Fisher CaO and NaOH left only 24% insoluble matter, outperforming the CaO freshly prepared from the hydroxide/NaOH combination (30% insolubles). We had suspected that the surfaces of the oxides that had been exposed to the atmosphere might have been substantially converted to inactive carbonates. The best results for the magnesium system were obtained with the combination of Magox and NaOH. Magox is a high surface area (~ 100-200 m²/g) MgO powder that is about 98% pure. The principle impurities are CaO and SiO₂. The combination of Magox with NaOH left only 26% insoluble matter compared to 32% for the NaOH/ freshly prepared MgO combination. The combination of NaOH with Fisher MgO performed very poorly, leaving 58% insoluble material. Calcining the Magox powder appeared to slightly reduced its efficiency, increasing the insolubles for the NaOH/Magox combination to 30%. This minor change may have been due to a loss of surface area upon calcination. Additional characterization of the Mg and Ca bases would be necessary to draw meaningful conclusions as to the reasons the materials perform differently. However, it is reasonable to assume that variables such as surface area (particularly for the Magox), impurities, and different preparation conditions (resulting in different quantities and strengths of basic surface sites) play a role.

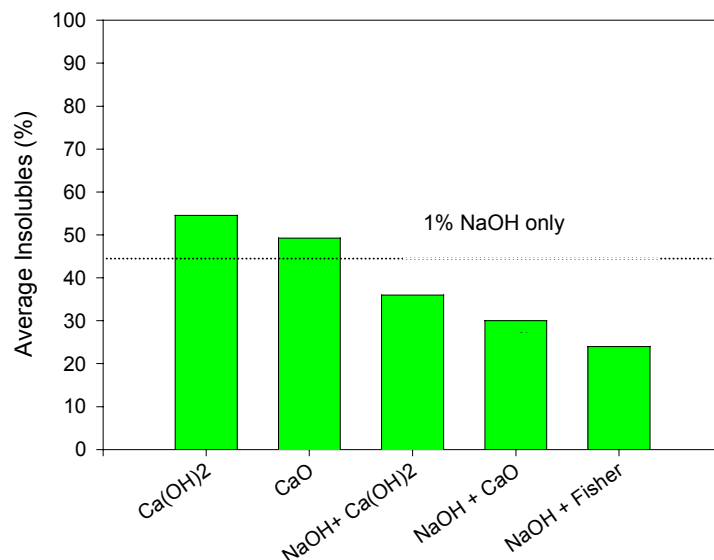


Figure 9. Lignin conversion (shown as insolubles remaining) in the presence of calcium bases (0.0106 OH⁻ equivalents) and calcium bases (0.0091 OH⁻ equiv.) combined with NaOH (0.0015 OH⁻ equiv.). The dashed line is the level of insolubles for 0.0015 equiv. of NaOH alone. CaO obtained by calcining Ca(OH)₂ or from Fisher Scientific.

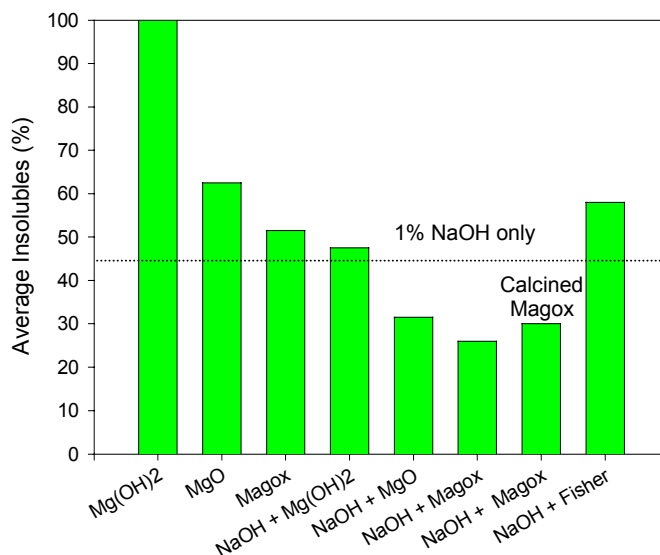


Figure 10. Lignin conversion (shown as insolubles remaining) in the presence of magnesium bases (0.0106 OH⁻ equivalents) and magnesium bases (0.0091 OH⁻ equiv.) combined with NaOH (0.0015 OH⁻ equiv.). The dashed line is the level of insolubles for 0.0015 equiv. of NaOH alone. MgO obtained by calcining Mg(OH)₂, from Premier Services Corp. (Magox) or from Fisher Scientific.

3.4.2 Effect of Aging CaO and MgO: As described above, the preparation of CaO and MgO by calcination should lead to the decomposition of carbonates. Thus, exposure of

CaO and MgO surfaces to the atmosphere could lead to changes in performance due to the uptake of CO₂. We tested the susceptibility of the CaO and MgO samples freshly prepared from the respective hydroxides to this effect by storing samples of the materials in contact with air for two weeks and then repeating the depolymerization experiments that were run immediately after the preparation. The results are shown in Figure 11.

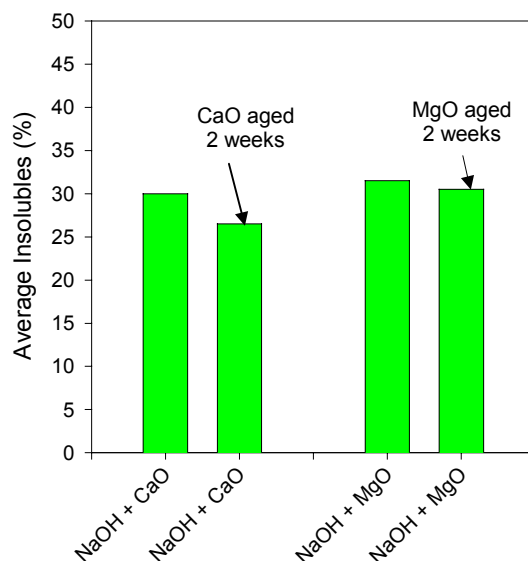


Figure 11. The effect of short-term aging of CaO and MgO prepared from the hydroxides on lignin conversion. Conditions were the same as those in Figures 9 and 10.

Figure 11 shows that the oxide samples exposed to the atmosphere for two weeks showed no degradation in performance. In fact, there appears to be a moderate improvement in performance, particularly for the CaO sample. This is consistent with the results presented in the previous section, where the best results were obtained over the as-received commercial CaO sample from Fisher Scientific. One possible conclusion is that CO₂ uptake by the oxide is relatively slow or in some cases may even have a moderate beneficial effect. Of course it is also possible that the effect of exposure to atmospheric CO₂ is very rapid. That is, it is possible that the results were similar in all cases because the uptake occurred during the time the samples were allowed to cool prior to the initial experiment.

3.4.3 Effect of Calcination Temperature: As described above, CaO and MgO was prepared for our baseline studies by calcining the respective hydroxides at 500°C. This temperature was based on reports in the literature that this activation procedure gave CaO catalysts with optimum basicity and activity. However, since the activation is thought to result from the removal of H₂O, CO₂, and O₂ from the CaO/Ca(OH)₂ surface, it is uncertain that these results are applicable to our system. Since the materials were ultimately placed back in an aqueous environment, the main chemical effect of the calcination should be the destruction of carbonates. However, as presented in section 3.4.2 we found that a two week exposure of one of our CaO catalysts to the atmosphere (including CO₂) did not significantly alter its performance. Furthermore, the best

performing CaO catalyst was a commercially prepared CaO from Fisher Scientific that had undergone no special activation procedure. Hence we suspected that the performance of CaO prepared from $\text{Ca}(\text{OH})_2$ would be somewhat independent of the calcination temperature. Similar observations were made for the MgO system, and thus we also suspected that the performance of MgO prepared from $\text{Mg}(\text{OH})_2$ would be independent of temperature.

To test our hypothesis, we calcined Fisher $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ at several temperatures and tested them for lignin depolymerization in conjunction with NaOH. The reactions were carried out at standard conditions of 290 °C, 1 hour reaction time, and a 10:1 water:lignin ratio (~ 0.6 g lignin). NaOH was used in conjunction with the other bases as a 1% (w/w) solution (0.0015 moles of NaOH in the reactor). About 0.009-0.010 moles (OH^- equivalents) of CaO or MgO was used. The results of the reaction tests are shown in Figure 12.

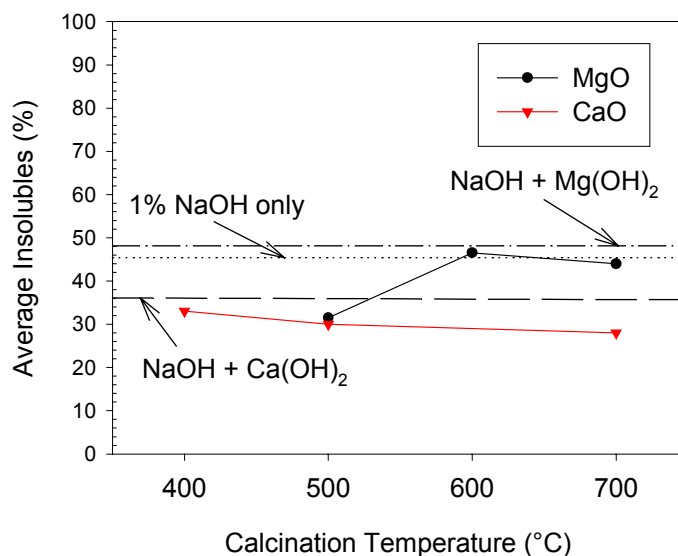


Figure 12. The effect of CaO and MgO (prepared from hydroxides) calcination temperature on Repap lignin conversion. The solid oxides (0.009-0.01 OH^- equivalents) were used in conjunction with 1%NaOH (0.0015 equiv.) at 290 °C for 1 hour with a 10:1 water: lignin ratio. For comparison, the dotted line is the level of insolubles for 0.0015 equiv. of NaOH alone, the dashed line is the level for 0.0015 equiv. of NaOH plus 0.009 equiv of $\text{Ca}(\text{OH})_2$, while the dot and dash line is the level for 0.0015 equiv. of NaOH plus 0.009 equiv of $\text{Mg}(\text{OH})_2$.

The data in Figure 12 are consistent with the expectation for CaO. Lignin conversion is almost independent of calcination temperature. Further, the calcined material is at best only 10% better than the parent $\text{Ca}(\text{OH})_2$. This is also consistent with the notion that the CaO rehydrates in the reactor to once again form a $\text{Ca}(\text{OH})_2$ much like the parent material. The data for MgO are harder to rationalize. The material calcined at 500 °C is clearly superior to those calcined at higher temperatures and the parent $\text{Mg}(\text{OH})_2$. This suggests that MgO calcined at 500 °C rehydrates to a form that is somehow different from the parent $\text{Mg}(\text{OH})_2$. On the other hand, the materials calcined at 600 and 700 °C

appear to be similar to the parent material. Alternately, they could be more like the 500 °C material but have lost activity due to a decrease in surface area or some other effect. In any case, the result is at least consistent with observations in the literature for CaO and MgO that basicity and activity decrease above an optimum calcination temperature, albeit for non-aqueous chemistry. It is also consistent with the previous observation that calcining the Magox sample decreased its performance (Figure 10).

3.4.4 Kinetics of NaOH/CaO Systems: Several experiments were conducted to determine the effect of CaO addition and temperature on the reaction kinetics. Based on the results for different CaO samples presented above, CaO as-received from Fisher was chosen as the baseline material to combine with NaOH. Reactions were carried out at 290, 310, and 330 °C using standard conditions (0.59 g Repap Alcell lignin, 10:1 solvent:lignin ratio, 1% NaOH solution (0.0015 moles OH⁻ in the reactor), and 0.0091 OH⁻ equivalents of solid base in an 8 ml reactor) with the following exceptions. Of the two reactions that were run at 290 °C, the amount of CaO was double the standard amount in one case, and about ¼ of the standard amount in the second case.

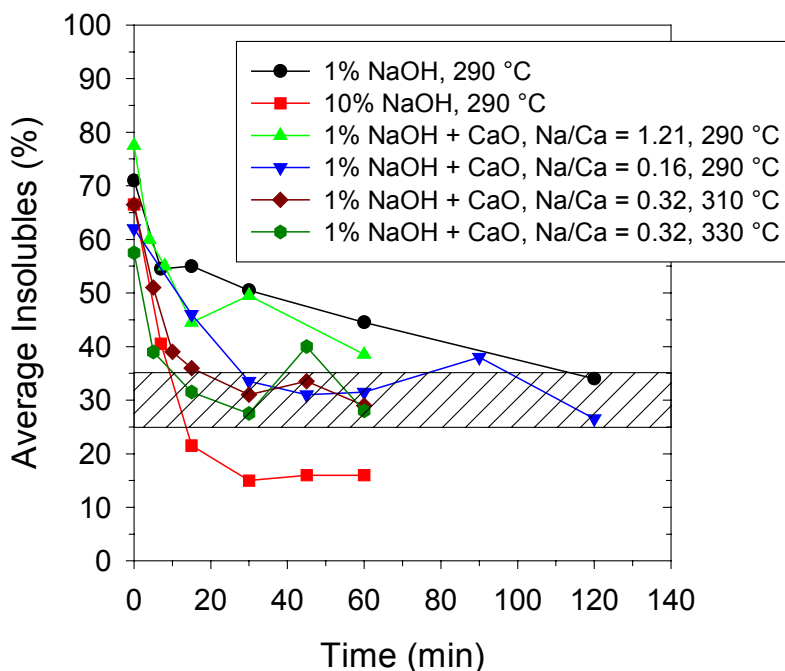


Figure 13. The addition of CaO and increased temperatures improve the kinetics of Repap lignin conversion in aqueous NaOH. However, an excess of NaOH is required to achieve the maximum conversion of lignin to water and ether solubles. (all data taken at 10:1 solvent:lignin weight ratio).

As shown in Figure 13, the kinetics of the 1% NaOH system can be improved through the addition of CaO or by increasing the reaction temperature. In all cases with CaO, the insolubles are minimized within at least the first 45 minutes. However, this is still slower than the 10% NaOH case. Furthermore, regardless of CaO concentration, or reaction temperature, the 1% NaOH system encounters an apparent limit to conversion so that 25-35% of the original lignin remains insoluble, about twice that for the 10% NaOH case. Interestingly, at longer times the insolubles show increases followed by decreases back to

the minimum values. The reason for this is not known, but similar behavior was seen in some of the previous studies conducted in alcohol solvents [13].

3.4.5 Effect of CaO Concentration: In the previous section we indicate that the ultimate extent of lignin conversion is independent of the CaO concentration, even though the addition of CaO effects the kinetics of the conversion. In order to verify this observation, we conducted a series of experiments at the standard reaction conditions, with the exception that the amount of CaO added to the reactor varied from 0 to 0.52 g, about twice the standard amount. The results of these experiments are summarized in Figure 14. As earlier results had indicated, the extent of lignin conversion as measured by water and ether solubility is independent of the CaO concentration. There were, however, some qualitative differences noted in the reaction products. The products of the reactions conducted with 0, 0.015, and 0.0309 g of CaO were difficult to recover from the reaction vessel as the solids tended to adhere to the reactor walls. The products of the reactions conducted with 0.064, 0.128, 0.254, and 0.515 g of CaO were easily washed out of the reactors. The precipitates recovered from these high CaO loading samples tended to become “sticky” when extracted with ether, and required more ether extraction cycles to reach an endpoint than did the precipitates from the low loading samples.

A close observer might notice that the conversion for 1% NaOH alone (no CaO addition) given in Figure 14, is about 34% rather than the 46% shown in Figure 6, for example. We attribute this to the greater experiment to experiment variability experienced for the aqueous system as discussed in Section 2. We also note that conversions are consistent with the apparent 25-35% limit shown in Figure 13.

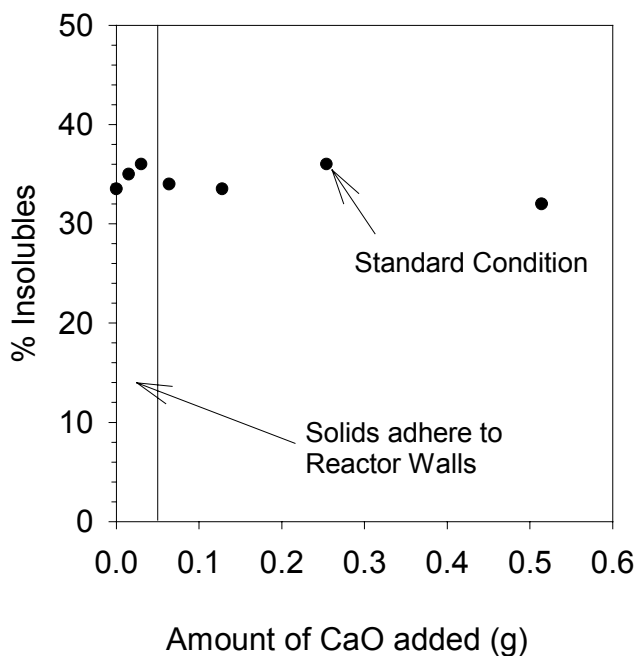


Figure 14. The ultimate degree of lignin conversion is independent of CaO concentration. (1% NaOH, 290 °C, 1 hour, 10:1 solvent:lignin by weight, CaO from Fisher)

3.4.6 Role of CaO in Mixed Catalyst System: As shown above, CaO hydrates and behaves as $\text{Ca}(\text{OH})_2$ in our system (Figure 12). Why then, do the two hydroxides, NaOH and $\text{Ca}(\text{OH})_2$, act synergistically to improve the reaction kinetics? A related question is why is the maximum conversion in 1% NaOH less than the maximum conversion in 10% NaOH? In the alcohol solvent systems, we were able to link a similar effect to formation of organic acids in the system (from the alcohols). The CaO appears to act as a sacrificial base, neutralizing the acids and allowing the reaction to be catalyzed by the NaOH [13]. Although such an effect couldn't arise from the solvent in the aqueous case, it seemed plausible that products from the depolymerization reaction (e.g. phenols and catechols) could slowly change the pH of the reaction media, thereby affecting the degree and rate of conversion.

To test this hypothesis, we first performed a series of simple experiments to evaluate the pH of the reaction mixtures before and after reaction. Experiments and blanks were performed in duplicate at the standard conditions (290 °C, 1 hr, 0.6 g Repap lignin, 10:1 water:lignin) with NaOH only, CaO only, and a combination of the two (0.0015 equiv NaOH, 0.009 OH^- equiv CaO). The duplicates were combined to create samples large enough for the pH probe. The results are shown in Figure 15.

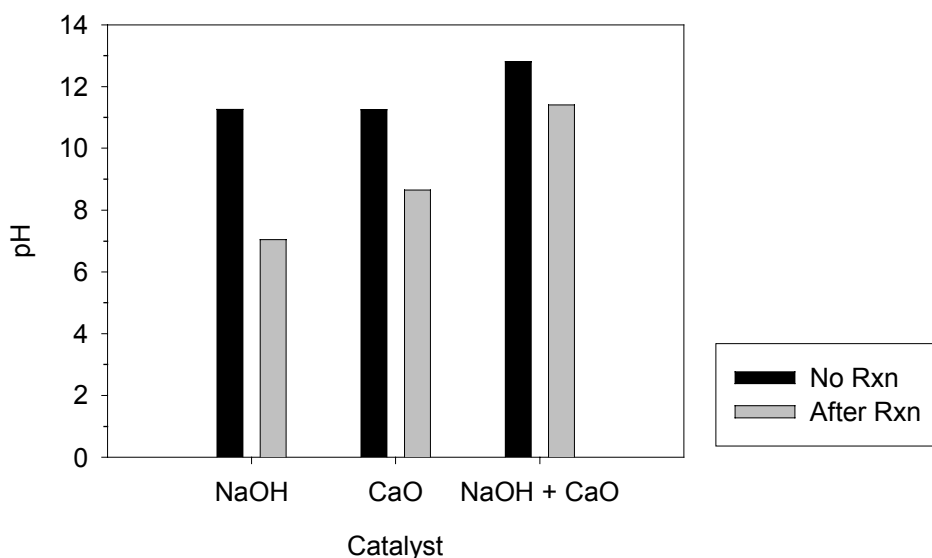


Figure 15. The pH of various reaction mixtures with and without heating for 1 hour at 290 °C. Only the combination of NaOH and CaO maintains a high pH. Experiments and blanks were performed in duplicate at the standard conditions (290 °C, 1 hr, 0.6 g Repap lignin, 10:1 water:lignin) with NaOH only, CaO only, and a combination of the two (0.0015 equiv NaOH, 0.009 OH^- equiv CaO). The duplicates were combined to create samples large enough for the pH probe.

Clearly, neutralization of the base catalysts is occurring to a much greater extent in the single base systems than in the combined system. In the NaOH case, the pH after reaction is neutral (7.04 measured), while in the case of CaO (which should have greater capacity) the pH is also nearly neutral (8.65) after reaction. Only in the combined case

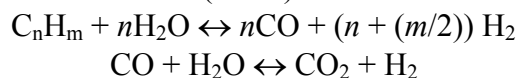
does the pH remain high (11.4). Interestingly, the total amount of OH⁻ in the combined system is only about 17% larger than in the CaO only system. Yet there is a drastic difference in the pH after reaction. One possible explanation is that in the system containing only CaO, only part of the base capacity (perhaps the surface) is utilized, while in the combined system, more of the base capacity is being accessed.

Figure 15 verifies that the aqueous system is like the alcohol system in that the combination of NaOH and a calcium base act in concert to keep the pH high. However, since the combination of CaO with NaOH increases the rate of conversion, but not the extent of conversion, the concept of CaO acting as a sacrificial base is clearly too simple in this case. A complex picture in which lignin conversion depends on both the OH⁻ and Na⁺ concentrations may be more accurate. In the presence of lignin depolymerization products, CaO is able to provide OH⁻ ions (as evidenced by the high pH after reaction), but may be unable to prevent the consumption of Na⁺ ions. Thus, the rate remains higher than it would if both OH⁻ and Na⁺ were being consumed, but ultimately falls to zero when all the Na⁺ is consumed by the lignin.

3.4.7 Acid Formation in the Mixed Catalyst System: Having verified that CaO acts to maintain high pH in the reaction media, we next addressed the question regarding the types of acid functionalities that were responsible for neutralizing the reaction media. Since the neutralization arise from products of the lignin depolymerization, potential culprits include phenols and catechols, organic acids, or even CO₂. CO₂ was carefully considered, since our collaborators reported significant evolution of gasses from reaction mixtures as they were acidified (in some cases these gasses were captured and identified as mostly CO₂) [20]. In our studies, gas evolution was observed on opening the reactor vessels, but was generally negligible upon acidification. However, we have experimentally verified that, at our concentrations, the amount of gas evolved from a neutralized reaction mixture could easily go unnoticed.

There are several potential sources of CO₂ in the reactor. First, there is some head space in the reactor containing ambient air when the fittings are sealed. Under reaction conditions, the O₂ from the air would be expected to oxidize the lignin to CO₂ and H₂O. However, one can easily show that, at most, this would result in only a few percent of the NaOH present in a 1% NaOH solution being neutralized, even if all the O₂ went to CO₂.

The second potential source of CO₂ is a steam reforming (SR) reaction of the lignin followed by the water gas shift reaction (WGS):



Although the equilibrium constants do not favor the reactions at low temperatures (Tables 1 and 2), consumption of the CO₂ by the base would tend to drive the reactions forward. Further, there are two materials in our system with known potential to catalyze the reforming reaction. As early as 1868, steam reforming was reported to occur over CaO (CO₂ reacts to form CaCO₃), and as early as 1889 over nickel (Inconel 600 is 80% nickel). Therefore, although probably unlikely, CO₂ formation through reforming pathways can not entirely be dismissed as possibility.

Table 1: Thermodynamic equilibrium constants for steam reforming of methane (SR), the water gas shift reaction (WGS) and steam reforming followed by the shift reaction (SR-WGS).

Temperature °C	SR	WGS	SR-WGS
100	2.6×10^{-18}	3700	9.5×10^{-15}
200	4.6×10^{-12}	240	1.1×10^{-9}
300	6.5×10^{-8}	41	2.6×10^{-6}
400	5.8×10^{-5}	12	7.2×10^{-4}

Table 2: Thermodynamic equilibrium constants for steam reforming of ethane (SR), the water gas shift reaction (WGS) and steam reforming followed by the shift reaction (SR-WGS).

Temperature °C	SR	WGS	SR-WGS
100	3.5×10^{-26}	3700	4.8×10^{-19}
200	1.2×10^{-15}	240	6.8×10^{-11}
300	1.2×10^{-8}	41	1.9×10^{-5}
400	1.1×10^{-3}	12	0.17

A third possible source of CO₂ is from the lignin itself, e.g. from carboxylate functionalities.

In order to experimentally address the issue of acid formation, we first undertook a series of experiments that were designed to explore the kinetics of the neutralization reaction. These experiments were modeled after those we successfully performed for conversion of methanol and ethanol to organic acids [13]. Reactions were performed under standard conditions (290 °C, 0.6 g Repap lignin, 10:1 water:lignin) with NaOH only, and a combination of NaOH and CaO (0.0015 equiv NaOH, 0.009 OH⁻ equiv CaO) for times of 0, 7.5, 15, 30, and 60 minutes. Following the reaction, the reaction mixtures were filtered through a 0.45 micron syringe filter. Then, a 0.2 ml sample of the filtrate was diluted with 25 ml of DI water and titrated with 0.1 N HCl utilizing a Mettler DL70ES autotitrator.

The results of these titrations were telling. Each titration consumed a similar amount of HCl, and only a single equivalence point was detected. That is, we were unable to discern free hydroxide ion (NaOH) from the conjugate base of the acid that had neutralized the NaOH. This indicates that the acids that are responsible for neutralizing the base catalyst in the aqueous system are weak acids (with strong conjugate bases). This first proton dissociated from carbonic acid is a relatively strong acid (pK_a H₂CO₃ = 6.37, 10.25) compared to phenol (pK_a = 9.99). Recall that in our previous work we were able to discern NaOH from sodium formate (pK_a formic acid = 3.75) and sodium acetate (pK_a acetic acid = 4.75) by titration with HCl [13]. Therefore, although we were unable to follow the kinetics, this titration study strongly suggests that it is weak acid products of lignin depolymerization (e.g. phenols), not CO₂, that neutralize the base.

To convince ourselves that phenols could be responsible for the base neutralization, and that CaO could act to prevent this neutralization, we performed an additional set of

experiments. We made three simulated reaction mixtures and measured their pH values. The first model was simply the standard 1% NaOH/lignin reaction mixture. As expected the pH of this mixture was 12.5. The second model simulated the condition after the reaction had proceeded to the point to produce enough phenol to neutralize the NaOH. This condition was modeled by replacing 23% (by weight) of the lignin in the standard mixture with phenol. The pH of this mixture was 10.4. The final model simulated the condition when the same conversion had been reached as in the second model, but when CaO was used in addition to NaOH. This mixture contained the standard ratios of water, lignin, NaOH and CaO, with the exception that 23% (by weight) of the lignin was replaced with phenol as for the second model. The pH of this mixture was 12.4. Thus, this series of models clearly demonstrates that phenolic products of lignin depolymerization can at least partially neutralize NaOH, and that CaO can act to limit this neutralization.

Our experiments provide indirect evidence that weak acid products of the lignin depolymerization are responsible for neutralizing the reaction mixture. In contrast, David Johnson at NREL has developed strong direct evidence for the production of CO₂ in the reaction, at least under certain conditions [17]. However, we will show below that CaO acts as a strong getter for CO₂, and thus large amounts would be necessary to neutralize the mixture. Given these conflicting results, we tentatively conclude that it is likely that both CO₂ and weak acid products are produced during lignin depolymerization, and that each plays some role in neutralizing the reaction mixture.

3.4.8 Solubility of CaO: If CaO were to be used to improve the reaction kinetics of an aqueous depolymerization scheme, there are several scenarios for adding it into a process. For example, a fixed bed arrangement might be utilized, or as an alternative a slurry feed could be used. Potential problems with the fixed bed arrangement loss of the CaO due to dissolution, plugging due to solids formation, or deactivation of the CaO surface. CaO dissolves in water as Ca(OH)₂, and the solubility of calcium hydroxide in water decreases from 0.185g/100 ml to 0.077g/ 100ml as the temperature increases from 0 °C to 100 °C. Thus one can anticipate that leaching of Ca from a fixed bed in the form of Ca(OH)₂ would be a relatively slow process. However, there are other interactions to consider.

We have shown that as the lignin depolymerizes, acidic functionalities are formed as reaction products. These acidic functionalities neutralize NaOH, or CaO (Ca(OH)₂) if it is present in the reaction mixture, presumably by forming Na or Ca salts. If Ca acts as a sacrificial base in the system as proposed, and if the calcium salts are soluble, it is possible that for every two moles of acid formed by lignin depolymerization, one mole of CaO will solubilized. Alternately, insoluble calcium salts may plug the bed or deactivate the CaO surface. For a fixed bed arrangement, a slow dissolution of some of the calcium is probably preferable plugging the bed with insoluble salts or deactivating the CaO surface with adsorbed acids.

In order to better understand interactions of calcium in the system, we performed a quick set of experiments that measured the amount of Ca in solution as a function of treatment. Three mixtures were prepared in duplicate, filtered with a 0.45 micron syringe filter, and

then analyzed for Ca ion by atomic absorption spectroscopy (AA). The first solution was simply a 1% NaOH solution with the standard ratio of CaO added. The second solution was a duplicate of the first, however it had been treated at 290 °C for 1 hour in the batch microreactors. The average calcium content of the second solution was less than half that of the initial solution. This is consistent with the expectation that Ca is less soluble at higher temperatures. However, there was a large variability between duplicates of the second solution. This variability is likely due to problems with the methodology. Since the batch microreactors do not provide a method to sample the hot solution, the samples were taken after the solutions had cooled. During the time it took to cool and sample the solutions, the Ca ion concentration was probably increasing back to the room temperature equilibrium value.

The final set of samples was a standard reaction mixture (including lignin) that had been heated to 290 °C for 1 hour. The final calcium concentration of these samples was comparable to the second set of samples, but again was highly variable. This variability could also be the result of deficiencies in the experimental methodology. These initial results do suggest however that at least at room temperature, the interaction between the organic and the CaO does not lead to the formation of soluble (at least at room temperature) Ca salts. However, without further study, we can not know whether reaction products were neutralizing the CaO surfaces. Nonetheless, a fixed bed arrangement appears to be less practical than other possibilities such as a slurry feed.

3.4.9 Preparation and Analysis of Large Sample: A single large sample of product from our batch microreactors was prepared for detailed analysis by David Johnson at NREL. The sample was prepared by combining the products from 39 duplicate reaction runs carried out at 330 °C for one hour. Each of the runs used about 0.59 g of Repap lignin, 0.255 g of CaO, and 5.9 g of 1% NaOH (0.0106 mols total OH⁻ equivalents, equivalent to about a 7% loading of NaOH). For comparison, there were approximately 0.0033 moles of lignin monomer units in the reactor (assuming a molecular weight of 180 g/mol for the monomer). Hence there was about a 2:1 ratio of lignin monomers to Na atoms, but more than a 3:1 ratio of OH⁻ equivalents to lignin monomers. After reaction, the contents of the reactors were recovered with DI water, acidified to a pH of 2, and combined.

The combined acidified samples were sent in three bottles without further treatment to NREL for workup and analysis. The following paragraphs extracted from an email written by David Johnson describe the workup of the samples and initial results.

All 3 bottles sent from Sandia were combined and worked up using our standard procedure. The pH of the solution was checked prior to the work up and found to be 1.7 so no further acid was added.

Work up procedure

The insoluble solids were filtered from the solution.

The solids were air-dried overnight and then extracted overnight in a soxhlet extractor using diethyl ether. The extract ran clear at the end of the extraction.

The ether extract was dried over anhydrous magnesium sulfate and then evaporated on a rotary evaporator.

The insoluble solids remaining after soxhlet extraction were air-dried over the weekend.

The aqueous solution was extracted with diethyl ether in a liquid-liquid extractor overnight. Both the extract and aqueous were almost colorless at the end of the extraction.

The ether extract was dried over anhydrous magnesium sulfate and then evaporated on a rotary evaporator.

Results

The results from the extraction are shown below. The yields are based on the total weight of lignin feed (22.96g). The yield of insolubles is close to the value (28%) shown in your report dated May 7th, 1999, (Figure 6). You will notice that we can only account for 83% of the lignin that was used. I presume that the remainder of the mass was lost as gases, volatiles and some mass transfer losses. Overall we have 53% of usable organic product that could be used in the subsequent HPR stage.

Recovery %	19.2g	83%
% Total Extract	12.1g	53%
% Soxhlet extract	6.8g	29%
% Aqueous extract	5.4g	23%
% Insoluble	7.0g	31%

As pointed out by David, the % insolubles is consistent with previous batch microreactor data. The 17% figure for losses is a little higher than anticipated but is within reason. Assuming a 5% loss to gas and volatiles would mean 12% recovery loss. Under the test conditions it has been noted that there is some material, that is difficult to recover from the reactor walls. We had estimated this unrecovered material to be no greater than 10% of the initial charge. Larger batch reactors, with a smaller surface to volume ratio, would likely lead to increased recovery. However, the behavior of the material under realistic flow conditions, e.g. in a packed bed reactor, is unknown.

3.5 Detailed Studies of Aqueous NaOH Catalyst System

3.5.1 Effect of Na:Lignin Ratio: Our initial studies of the aqueous NaOH catalyst system showed a strong correlation of conversion with the ratio of Na to lignin. A similar correlation was found in earlier studies with alcohol solvents [13]. Clearly, from an economic point of view, it is desirable to achieve a large conversion with a minimum amount of base. Therefore, a number of experiments were conducted with the aim of establishing the relationship, if any, between the NaOH concentration, the Na:lignin ratio, and the lignin conversion. Duplicate one hour reactions were carried out at 290 °C for 0.5, 1, 2, and 3% NaOH solutions. The experiments were repeated with the addition of the standard amount of CaO (0.23 g). The results of this testing are summarized in Figure 16, which presents the conversion as a function of the Na:lignin molar ratio (assuming an average molecular weight of 180 for lignin monomers). When presented in this fashion, it becomes apparent that the data collapses to a single trend represented by the curved line in the figure. A line marks the 10:1 lignin:NaOH ratio used in the standard experiments.

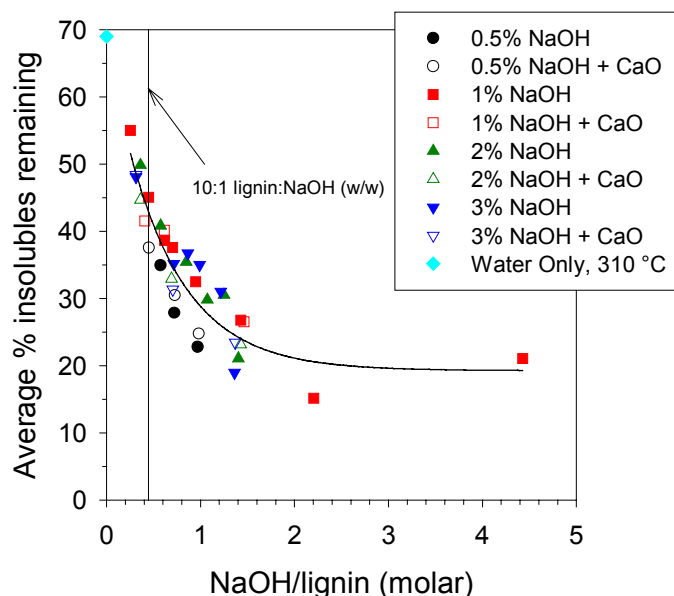


Figure 16. Na:lignin ratio is the primary factor governing lignin conversion for NaOH concentrations of 0.5 – 3% (w/w).

Figure 16 shows that the primary factor governing the extent of lignin conversion is the NaOH:lignin ratio. NaOH concentration, per se, is at best a secondary issue. In addition, Figure 16 shows that, from the stand point of conversion, the optimum ratio of NaOH to lignin is in the range of 1.5 – 2 (on a molar basis). Higher ratios do not lead to further increases in conversion. It is interesting to note that David Johnson's analysis of depolymerized lignin products indicates that there are on average 1.7 phenolic groups per phenyl ring [17]. This correspondence to the optimum ratio lends credence to the notion that acidic functionalities from the depolymerized lignin are responsible for deactivated (neutralizing) the base catalyst. Finally, Figure 16 confirms that the addition of CaO to the system does not appreciably alter the degree of lignin conversion (consistent with the data presented in section 3.4).

3.5.2 Effect of Water:Lignin Ratio (NaOH concentration): A number of experiments were performed in addition to those presented in Figure 16 to evaluate the effect of NaOH concentration (or water:lignin ratio) on conversion. Initially, a series of five experiments were conducted wherein the lignin:NaOH ratio was held constant at the standard ratio of 10:1 (w/w) for NaOH concentrations of 0.25, 0.50, 1.0, 2.0, and 3.0% (w/w). CaO (0.23 g) was added to each reactor, and a zirconia ball was included to improve mixing. The reactors were heated to 290 °C for one hour in the fluidized sand bath. Duplicate experiments were conducted for all cases. The results of the experiments are shown below in Figure 17. Due to a reactor leak only a single data point was obtained for the 2% NaOH case. The results for 0.25, and to some degree 0.50%, NaOH were much better than expected, yielding insolubles of only 16 and 24% respectively. Due to the surprising result for the 0.5% NaOH, the experiment was repeated three additional times; the result shown in Figure 17 represents an average of those five

experiments. For the case of 0.25% NaOH, the total amount of lignin being used was so small that any losses in transferring material may have been a large enough fraction of the total to significantly effect the final result, thus no additional experiments were conducted with 0.25% NaOH.

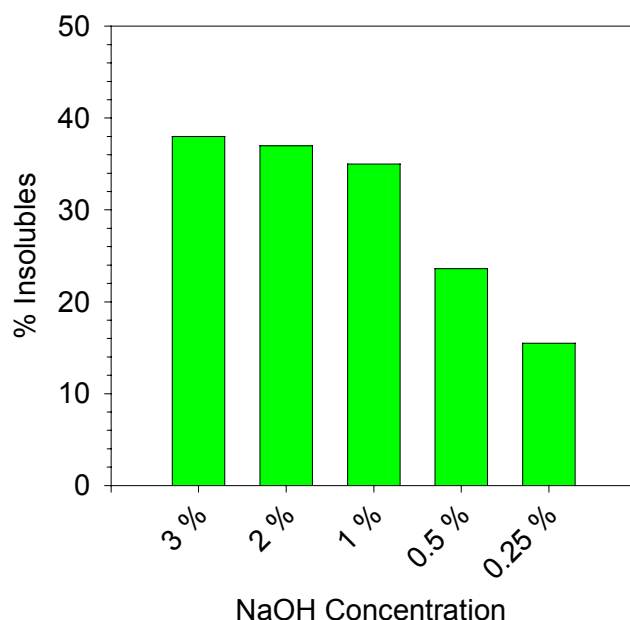


Figure 17. Very high dilutions may result in improved conversion.

A second series of experiments was conducted using higher concentrations of NaOH. In this case, the NaOH concentration was varied from 3 - 30 %. The results have been combined with data from Figure 16 for 1, 2, and 3 % NaOH and are presented in Figure 18. For the data presented in Figure 18, the NaOH:lignin ration varied from 1.4 to 4.4. Note, however, that in all cases the Na:lignin ratio is in the region where conversion should be maximized (Figure 16). The highest concentration of NaOH represented in Figure 18 is 20%. This is because at higher concentrations (30 % NaOH, NaOH:lignin = 2), the products of the reaction formed a thick paste that was extremely difficult to recover from the reaction vessel.

Figure 18 shows that the effect of water:lignin ratio is negligible, at least for reasonable NaOH concentrations (1- 20 % (w/w)) and optimized Na:lignin ratios. The data in Figure 17 is more ambiguous suggesting that there may actually be a positive effect at very high water:lignin ratios (beginning at about 0.5% NaOH) that may help overcome the apparent conversion barrier when Na:lignin ratios are less than optimum. However, one should keep in mind that, as the dilution increases, the cost of constructing and operating a reactor will eventually become impractical.

Nevertheless, the positive outcome for the 0.5 % (and 0.25 %) NaOH prompted additional investigations aimed at rationalizing the results. To this end, we performed a series of lignin solubility determinations in 1, 2, and 3% NaOH. The results, shown in Figure 19, provided a possible rationale for the data in Figure 17. Assuming the

extrapolation of lignin solubility down to 0 % NaOH is valid, Figure 19 shows that all the lignin in 10:1 solution is soluble at any NaOH concentration of 0.3% or less. Thus, one possible explanation for the results in Figure 17 is that at very low NaOH concentrations, lignin dissolution was complete, and lignin conversion was therefore enhanced.

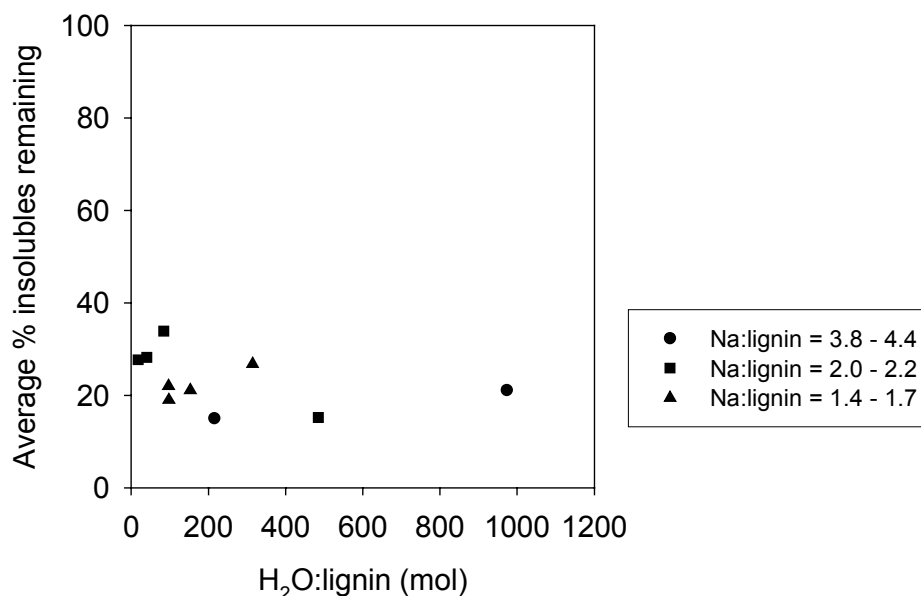


Figure 18. For optimum Na:lignin ratios and NaOH concentrations of 1-20% (w/w), the effect of H₂O:lignin ratio is minimal.

Unfortunately, there are at least two notable defects in this analysis. Namely, for convenience, we measured the solubility of lignin at room temperature, while our reactions were carried out at 290 °C. The solubility of lignin under reaction conditions is certainly more relevant to the question at hand. Since solubility typically increases with temperature, the room temperature values represent a worse case scenario. The actual solubility under reaction conditions may be significantly higher. Furthermore, as pointed out by David Johnson of NREL, our lignin is a mixture of different compounds, and our method of measuring solubility gives us the point where we have reached the solubility limit of only one or several of those compounds, and those may be minor components. The remaining fraction of lignin may have much greater solubility limits. In other words, although Figure 19 shows that the limit of complete solubility in 1% NaOH is about 6.5% lignin, it would be incorrect to assume that if we tried make a 10% lignin solution in 1% NaOH, that 65% of the lignin would dissolve and 35% would remain insoluble. In fact, almost all of the lignin would dissolve, leaving only a very minor fraction of insoluble material. Thus, under the conditions in question, solubility is probably not an issue.

This point is further illustrated by Figure 20. In this version of Figure 16, we have added a line demarking the approximate limit of complete lignin solubility. Lignin was initially completely dissolved by the NaOH at points taken to the right of line marking the solubility limit. To the left of the line, some of the lignin was initially insoluble in the NaOH. Clearly, the lignin solubility prior to reaction is not a significant factor in determining the overall level of conversion. If it were, the data might reduce to trend

line as it does in Figure 20, but the change in slope (the beginning of the flat part of the line) would be expected to begin at or near the solubility limit. This is clearly not the case. Assuming that the lignin solubility increases with temperature moves the lignin solubility line to the left, reinforcing this point.

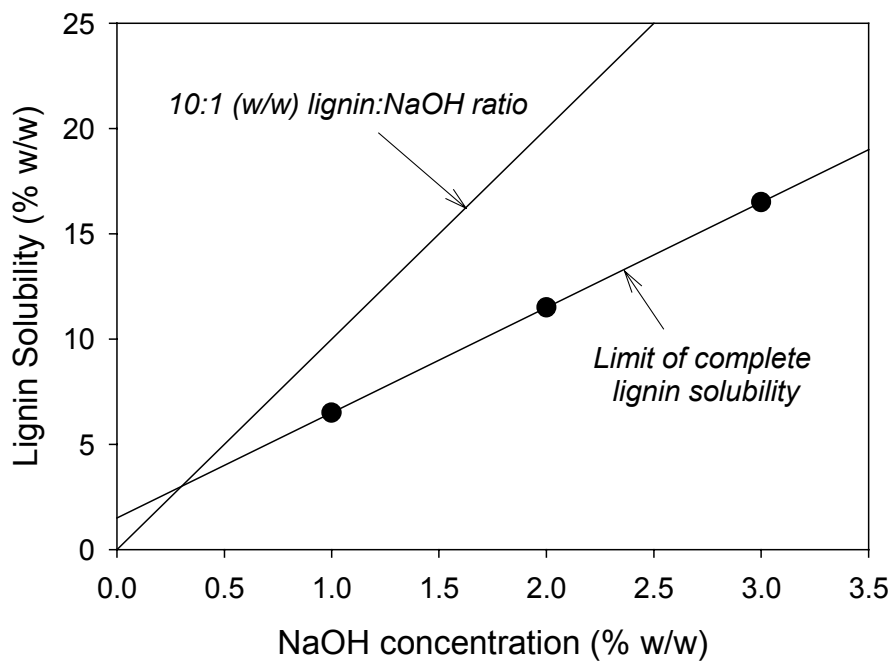


Figure 19. Lignin solubility in aqueous NaOH.

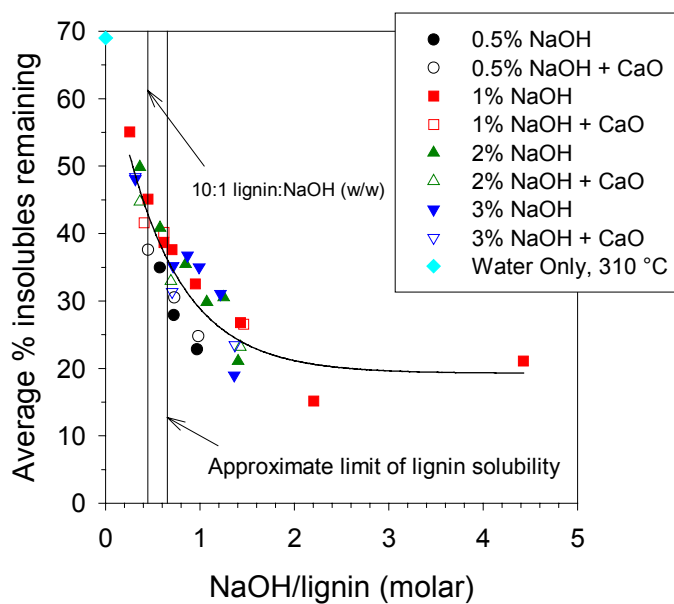


Figure 20. Lignin solubility does not determine conversion.

As a final comment we note that the 0.5 % data in Figure 16, is not completely consistent with the data in Figure 17. Close examination of Figure 16 reveals that the performance in the 0.50 % solution might be slightly better than that in the higher concentration solutions, but not to the degree indicated in Figure 17. This difference is difficult to rationalize, but is probably related to two factors. First, the experiments summarized in Figure 16 and Figure 17 were conducted by different people. As outlined in the experimental section, for unknown reasons, the variability has been greater when using water as a solvent than when using alcohol. One way we have attempted to address this has been to limit comparisons between data taken by different people since unknown aspects of the experimental technique probably play a role in this variability. Second, in this particular case, the difference in experimental techniques has probably been exacerbated by the relatively small total amount of lignin being used in conjunction with the 0.50 % NaOH.

3.5.3 Recycling Unconverted Lignin: A set of experiments was conducted to determine the fate of unreacted lignin. That is, if lignin were initially treated with a ratio of NaOH:lignin that was too small to get complete conversion, could we later recycle the unconverted lignin, or add additional NaOH to increase the conversion, or would retrogressive reactions occur to make this impossible? To answer this question, four reactions were run in duplicate. Since we intended to add additional material to one of the reactors, the conditions were slightly different from the standard, thus three control reactions were part of the experimental design. The first control reaction, conducted at 290 °C for 1 hour, combined 3.5 g of 1 % NaOH with 0.525 g of lignin (NaOH:lignin ratio = 0.3). From Figure 16, the expected outcome of this experiment was 45% insolubles, and indeed the experimental result was 42% insolubles. The second control reaction was identical to the first, except that it was allowed to proceed for 2 hours. Again the expected outcome of 45% insolubles closely matched the experimental result of 44% insolubles. Thus under the conditions of study, increasing the reaction time from 1 hour to 2 hours did not improve the overall conversion.

The third reaction was the one of interest, and it was carried out in two stages. The first stage lasted for 1 hour, and was otherwise identical to the two previous reactions. After the 1 hour had elapsed, the reactor was quenched and carefully opened. From the earlier results, we know that at this point 45% of the lignin remained as unconverted (insoluble) material. Then, 2 g of 10% NaOH was added to the material already in the reactor, increasing the NaOH:lignin ratio to 2. The reaction was then allowed to proceed for an additional 1 hour at 290 °C. Based on the final NaOH:lignin ratio, Figure 16 instructs that the insolubles remaining should be no greater than 23% of the original lignin mass. However, the experiment yielded a result of 37% insolubles. Since the second control experiment showed no increase in conversion, the increase in this case must be linked to the addition of NaOH. However, it appears that some of the original material was altered to an unconvertible state during the first stage.

In order to verify this alteration, a final control reaction was run. In this case, 3.5 g of 1% NaOH, 2 g of 10% NaOH, and 0.525 g of lignin (the same amounts cumulatively added in the previous case) were reacted for 2 hours at 290 °C. The experimental result was

28% insoluble material, not quite as good as expected, but significantly better than the test case. Therefore, we conclude that there could be some benefit in recycling unconverted lignin, but overall, less lignin would be converted than if the NaOH:lignin ratio were carefully controlled during the first pass.

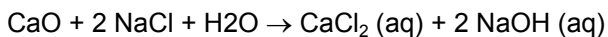
3.6 Alternate Sources of NaOH:

An ideal base driven depolymerization process would use a minimum amount of an inexpensive, readily available, and easily recyclable base. We have shown that when alcohols are used as the solvent, the highest conversions are obtained with a molar excess, relative to lignin monomer units, of strong bases such as NaOH, KOH and CsOH. High concentrations of inexpensive, weaker bases (Ca(OH)_2 and Na_2CO_3) result in poor conversions. Fortunately, in the alcohol case, a synergistic combination of a substoichiometric amount of NaOH and a larger amount of the less expensive Ca(OH)_2 can be used to achieve significant conversions. When water is used as a solvent, the addition of excess CaO (or Ca(OH)_2) improves the kinetics but not the overall conversion, even though the pH of solution remains relatively high. This suggests that, in some sense, both the anion (OH^-) and cation (Na^+) function play a role in the aqueous reaction chemistry. Following this reasoning, we performed several experiments in which we supplemented the OH^- concentration with CaO, and/or the Na^+ concentration with NaCl or Na_2CO_3 .

Recognizing the variability in our data that sometimes occurred over time, we began by running a duplicate set of control experiments under the standard conditions, including the addition of CaO. The result was an average of 25% insoluble material remaining after reaction. We then repeated the experiment as before, with the addition of 0.16 g of NaCl, enough to triple the Na^+ concentration in the reaction. The result was an average of 30% insoluble material remaining. Repeating the experiment with the addition of 0.16 g of NaCl, but the absence of CaO resulted in an average of 34% insoluble material. Carrying out the experiment with the addition of 0.48 g of Na_2CO_3 (increasing the amount of Na by a factor of more than 7), but with no CaO, resulted in an average of 30% insolubles.

Clearly the combinations employed had little or no effect on the lignin conversion. To understand this more clearly, we calculated the thermodynamic equilibrium constants for the reactions of interest, specifically focusing on the production of aqueous NaOH. An example of the results is shown in Table 3 below.

Table 3. Thermodynamic equilibrium constants calculated for the reaction

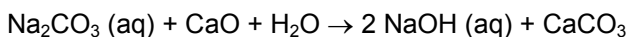


Temperature (°C)	Calculated equilibrium constant, K
0	1.22×10^6
100	54.6
200	.0588
300	3.24×10^{-4}

Although the results appear promising at low temperatures, the retrograde solubility of Ca (at 300 °C, $K = 6.6 \times 10^{-4}$ for the reaction $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$) results in small values for the equilibrium constant at the reaction temperature. Thus the effective concentration of NaOH that can be achieved using NaCl and CaO is very low unless large excesses are employed.

For comparison, we performed additional calculations for the combination of Na_2CO_3 and CaO. This combination is, of course, employed in Kraft pulping for the regeneration of caustic. Not surprisingly, in this case, the results were very promising (Table 4).

Table 4. Thermodynamic equilibrium constants calculated for the reaction



Temperature (°C)	Calculated equilibrium constant, K
0	1.6×10^{14}
300	2.4×10^7

Studies of lignin depolymerization using the combination of only Na_2CO_3 and CaO (No NaOH) confirmed the efficacy of this approach. Depolymerization reactions were carried out for one hour at 290 °C. The initial experiment employed the standard amount of CaO (0.0091 OH⁻ equivalents) and 5.5 ml of a 1.3% (w/w) Na_2CO_3 solution (equivalent to a 1% NaOH solution on a Na basis). The standard 10:1 ratio of lignin:Na (on a NaOH w/w basis) was maintained. Two additional reactions were run in which the lignin:Na ratio (w/w) was adjusted to 2.6 and 1.2. The results are shown in Figure 21 along with the results previously presented in Figures 16 and 20 for comparison.

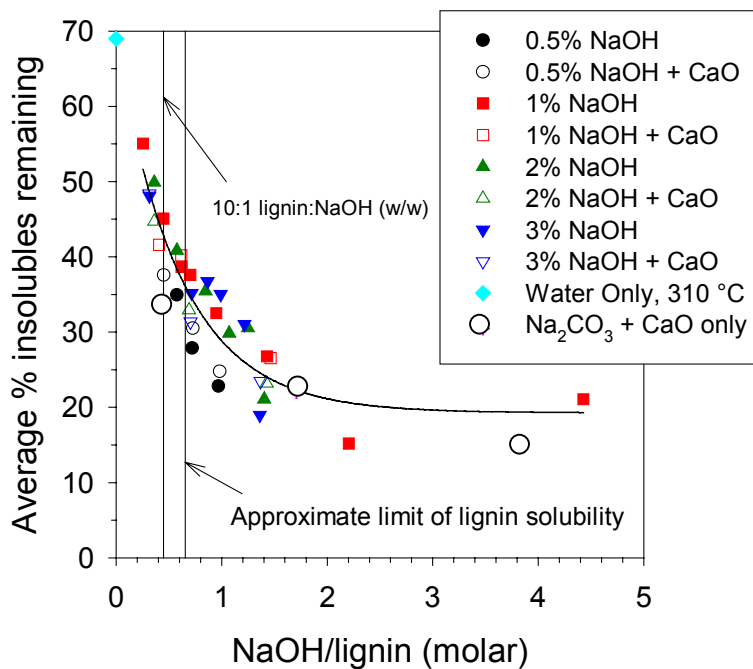


Figure 21. The combination of Na_2CO_3 and CaO mimics the performance of NaOH.

It is clear from Figure 21 that the combination of Na_2CO_3 and CaO performs similar to NaOH , as anticipated. A simple analysis of the economics of replacing NaOH with this combination also appears promising. Bulk chemical prices for NaOH , Na_2CO_3 , and CaO obtained from the web sites for Purchasing.com magazine (formerly free, now a pay site - www.manufacturing.net/magazine/purchasing/) and Allchem Industries (www.allchem.com) are given in Table 5. In the last row the price of NaOH produced from Na_2CO_3 and Ca(OH)_2 with a stoichiometric reaction is given. This simple analysis suggests, that even in the worst case where Na_2CO_3 and CaO are used on a once through basis, this alternative could lead to significant savings. A process where the precipitated CaCO_3 is recovered and regenerated (possibly in conjunction with burning the unconverted lignin waste) could offer further advantages, as could recovering the Na as Na_2CO_3 or NaHCO_3 by neutralization of the product solution with CO_2 (see below).

Table 5. Bulk Chemical Prices

Chemical	\$/lb	\$/lbmol
NaOH (flakes or beads)	0.18-0.28	7.20-11.20
Na_2CO_3 (soda ash)	0.038-0.044	4.03-4.61
Ca(OH)_2 (hydrated lime)	0.039	2.89
NaOH (calculated) soda ash + hydrated lime	0.087-0.094	3.46-3.75

As a final note to this section, the results achieved for the combination of Na_2CO_3 and CaO support our claim in the previous report that NaOH is neutralized in the aqueous system by weak acids derived from lignin rather than CO_2 or stronger acids. As the results show, if CO_2 were produced during the reaction, it would preferentially react with the CaO (or hydroxide) over the NaOH , allowing the reaction to proceed.

3.7 Process for Base Generation and Recycle:

Based on our earlier work, a complete process for base generation and recycle was proposed (Figure 22). As shown in the figure, the process revolves around the reaction of CaO with Na_2CO_3 to produce NaOH . After this reaction is carried out, the calcium can easily be recovered as the carbonate, since it is essentially insoluble in water (0.0015 g/100 ml at 25 °C). CaO is then regenerated from the carbonate through high temperature calcination.

The NaOH solution resulting from the central reaction is combined with lignin and the depolymerization reaction is carried out at elevated temperature, as usual. The products of the depolymerization reaction are then neutralized with CO_2 , rather than the standard HCl . Provided that this neutralization can be accomplished effectively, the result should be a solid precipitate containing depolymerized lignin fragments, and a $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ solution that also contains the water soluble fraction of the depolymerized lignin. Since Na_2CO_3 and NaHCO_3 have relatively high solubilities in water ($\text{Na}_2\text{CO}_3 = 7.1$ g/100 ml at 0 °C, corresponding to a 5.1% w/w solution of NaOH , and $\text{NaHCO}_3 = 6.9$ g/100 ml at 0 °C, corresponding to a 3.2% solution of NaOH), the precipitated lignin fraction is readily separated from the sodium salts via filtration. The water soluble

fraction could be recovered via solvent extraction. Depending on the recoveries of the various processes, the Na_2CO_3 solution could be recycled as is, or alternately dried and calcined to destroy any residual organics prior to recycle.

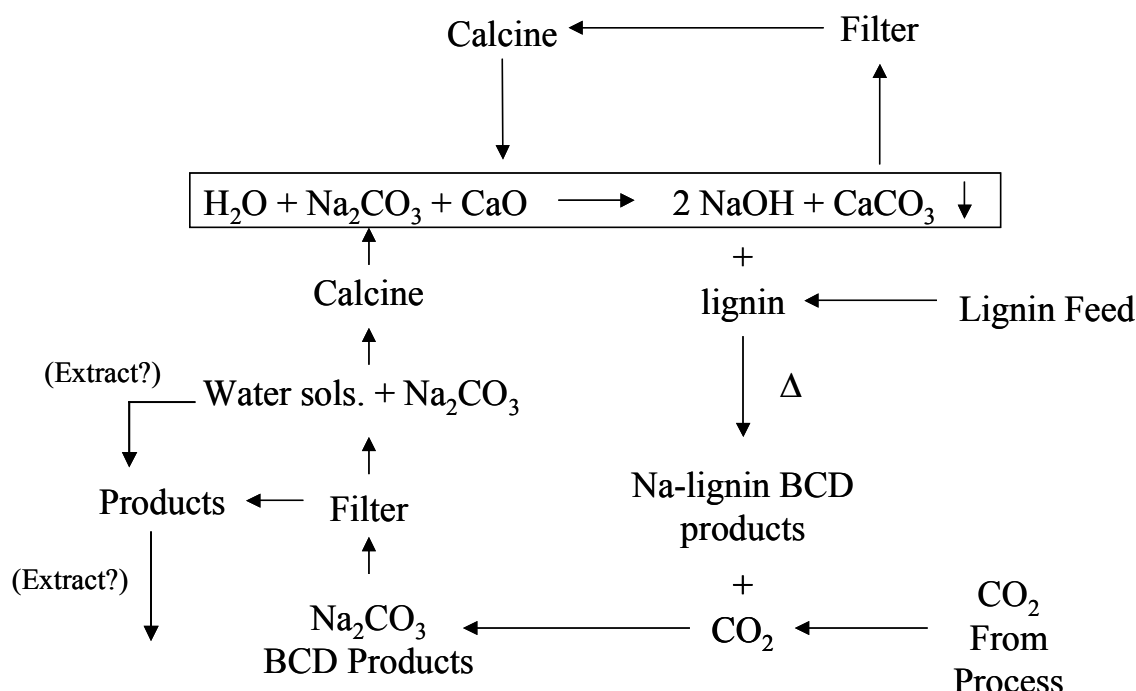


Figure 22. Proposed scheme for base generation and recycle.

Just prior to the end of this program, an experimental program was begun to validate the proposed process. As expected, the calcium recovery portion of the process is straightforward and results in essentially 100% calcium recycle. The remainder of the effort focused on the Na recovery portion of the process.

For our initial analysis, we considered a hypothetical mixture of reaction products produced with the aqueous depolymerization process. It should contain about 1% NaOH, 10% lignin depolymerization products (or salts resulting from the neutralization of the NaOH by the depolymerization products). Now, using Table 6 as a guide, we began to anticipate what would happen as CO_2 is bubbled through the hypothetical solution.

Table 6: Strengths of bases relevant to neutralizing the aqueous system with CO_2 .

Species	pK_b
NaOH	Strong base
CO_3^{2-}	3.75
$(\text{C}_6\text{H}_5)\text{O}^-$ (phenolate)	4.01
HCO_3^-	7.63

From Table 6, we anticipate that as CO₂ is added to the solution, the pH will fall as NaOH is converted to Na₂CO₃. Further CO₂ addition would begin to neutralize some of the organic salts and convert carbonate in solution to bicarbonate:



Ultimately, the organic salts would all be neutralized and precipitate, and finally carbonic acid would be formed.

A review of the literature was then conducted in an effort to identify the process conditions that would be required to achieve the anticipated steps in the neutralization. Several processes similar to the proposed process were identified and provided valuable information. One of the processes identified reacts high pressure liquid CO₂ with dissolved metals to form carbonates that can then be recovered as solids [21]. The other processes use CO₂ neutralization to recover casein from milk [22,23], or soy protein from a soy meal extract [24].

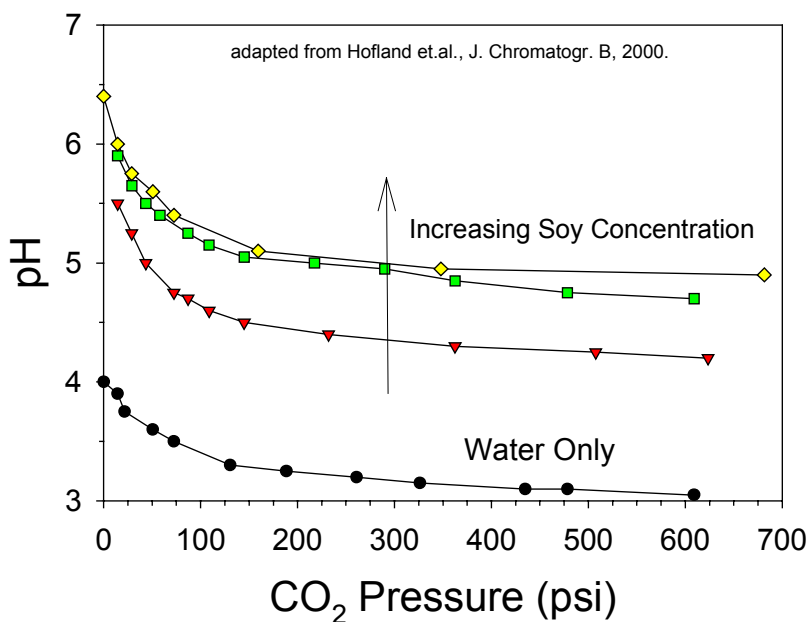


Figure 23. Relationship between CO₂ pressure and pH for a soy meal extract solution.

From a review of these processes, it was immediately evident that elevated pressures would be required to achieve the desired level of neutralization. For instance, the developers of the metals recovery process indicate that the pH of water exposed to gaseous CO₂ will reach a minimum of only about 5.5. In contrast, they report that water in contact with liquid CO₂ (1000-3000 psi, 25-70 °C) will reach a pH of 2.8-2.95 [21]. Similar trends are reported by the other authors, although there appears to be disagreement as to the pH values that are attainable under different conditions. We have adapted some of the data from Hofland et al. [24] for Figure 23 to illustrate several pertinent points. First, at lower pressures (< 150 psi), the pH is strongly dependent on the pressure. However, at higher pressures, the pH is only weakly tied to changes in the

pressure. Above the saturation pressure (940 psi at 25°C), the pH is almost independent of changes in pressure (not shown in Figure 23). Figure 23 also shows that the pressure required to reach any given pH is strongly dependent on the concentration of organics in solution, as is the minimum pH that can be achieved (due to the buffering capacity of the organics). For pure water in contact with pressurized, but gaseous, CO₂, a minimum pH of about 3.1 was observed. A final observation (not illustrated in Figure 23) is that the pH is virtually independent of the temperature.

A limited number of experiments, in which reaction mixtures (5% NaOH, 2:1 Na:lignin ratio, 290 °C, 1 hour) were neutralized with CO₂ and ambient pressure verified the expectations. The lowest pH achieved in any case with CO₂ was only 6.75. Yet, CO₂ neutralization did result in quantities of solids being precipitated out of solution similar to those resulting when the solution was acidified to pH 2 with HCl (roughly 55-65% of the original lignin mass after drying). However, it was clear that precipitation via CO₂ was incomplete, and that the resulting solids were different in character than those obtained via HCl acidification.

In the case of CO₂ precipitation, the water fraction remained dark, indicating the presence of dissolved solids, whereas a clear solution resulted from HCl acidification. Additional acidification (HCl, final pH=2) of a filtrate solution obtained from a CO₂ treated sample resulted in the precipitation of additional material equivalent to about 10% of the original lignin mass. In addition, the solids obtained via CO₂ neutralization could not be extracted with ether, whereas the HCl material was highly soluble, generally leaving about 20% insoluble material behind. Thus, it appeared that much of the material precipitated with CO₂ was in the form of Na salts.

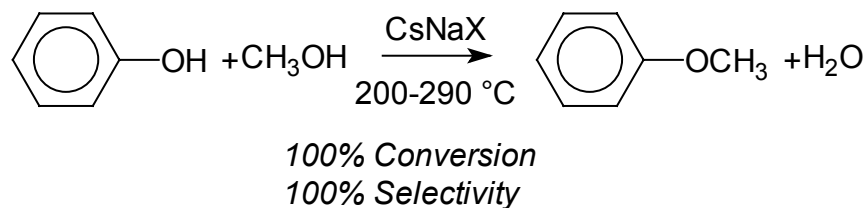
We attempted to verify this observation by performing a material balance on the Na throughout the complete cycle. This was done by calcining samples of the precipitated solids to burn off the organic fraction, and by collecting the water fractions, drying them, and calcining them. Probably due to the small size of the samples, and the fact that we did not analyze the inorganic materials left after calcination to verify their composition, the material balance did not close well (we appear to have collected more Na than we started with). However, there was clearly some ash left after calcining the precipitated material (amounting to less than 7% of its original mass prior to calcination) suggesting at least some of the material was in a salt form. Yet, it was also apparent that the overwhelming majority of the Na remained dissolved in the water fraction.

It is clear that the next step in developing the base recovery process is to proceed with the neutralization at elevated CO₂ pressures. To some extent this work can be done with only slight modifications to standard autoclave type reactors. Ultimately, however, a system specifically designed for this purpose would likely need to be developed and fabricated. This system would allow the precipitate to be recovered at pressure since the acid-base equilibrium will shift back towards the base as a function of time after the CO₂ overpressure is released. We were in the process of modifying an autoclave and beginning our pressure studies when this program was halted.

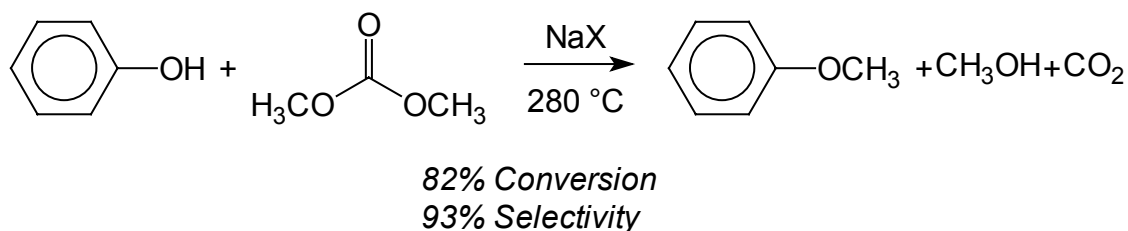
3.8 Model Compound Studies and Reaction Chemistry:

Model compounds studies were motivated by two factors. The first factor was a desire to identify the origins and types of acid functionalities produced by the depolymerization reaction and responsible for neutralizing the NaOH catalyst. It was hoped that, as in the case with alcohol solvents, this knowledge might suggest a path to prevent their formation. In addition, it was hoped that this information might point to differences between the work at Sandia and NREL that led us to conclude that weak acid functionalities are predominantly responsible for the neutralization, while NREL concluded that CO₂ was the predominant factor.

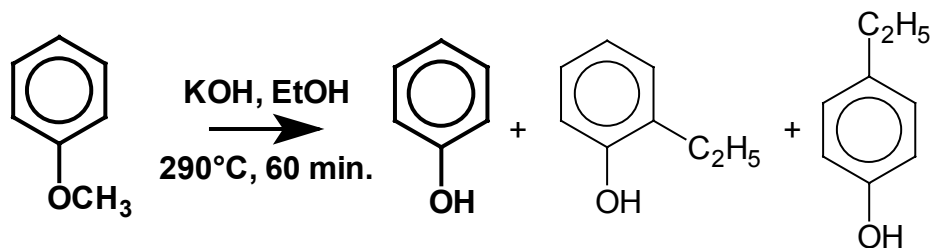
The second factor, related to the first, was the discovery of two publications concerning the selective O-alkylation of phenol over solid base catalysts. The first and potentially most significant report describes the reaction of phenol with excess methanol over a Cs-loaded large-pore zeolite to form anisole [25]. This reaction, shown below, is the reverse of the type of reactions that occur during lignin depolymerization with base in alcohol solvents, and presumably in aqueous solutions.



A similar reaction was observed over a sodium-loaded zeolite, but in this case the alkylating agent was dimethyl carbonate [26].

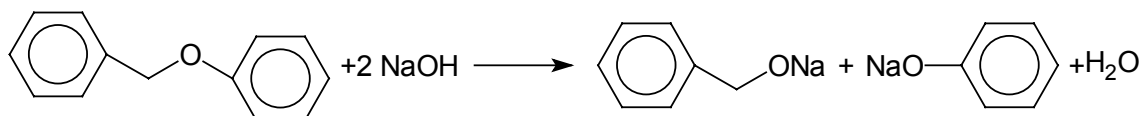


The most remarkable attribute of these reactions is the high selectivity to O-alkylation. In particular, for the methanol case, no ring alkylation was observed, even at 100% conversion. In our previous work with model compounds, we observed that anisole decomposed in the presence of KOH and ethanol to primarily produce phenol [13]. However, lesser amounts of ethyl phenols were also formed.

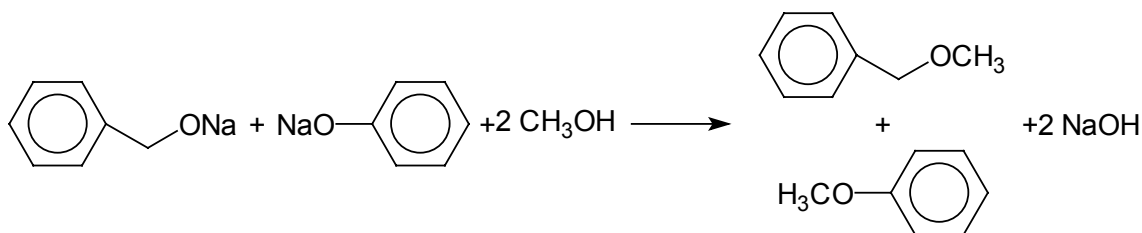


The published results raise some interesting questions, and suggest two interesting possibilities. First, we note that the forward and reverse reactions are both catalyzed by materials with some basic character, albeit in one case an alkali-metal loaded solid zeolite and in the other dissolved KOH. We do realize, of course, that dehydration reactions such as the one between methanol and phenol are commonly catalyzed by acids, suggesting that the acidic character of the zeolite might play a role in the reaction as well. Nevertheless, the results illustrate a reversible character for the reaction, and raise the possibility that under certain conditions the basic zeolites might catalyze the depolymerization reaction in an alcohol solvent without resulting in consumption of the alcohol through ring alkylation.

A second possibility, based on the observation that etherification is reversible, is the combination of depolymerization and etherification of the resulting phenols into a single step or closely coupled sequential steps with different reaction conditions. In this scenario, a base catalyst would first be used to cleave the ether structures in the polymeric/oligomeric lignin. Although this is potentially possible with both solid and soluble bases, a particularly interesting scenario develops if the results could be extended to the soluble base system (as shown in the next two reactions).



After reaction, the solution containing the base and the product phenolic groups (or phenolate ions) would then be exposed to different reaction conditions that would favor the formation of methyl (or ethyl ethers). These alternative reactions conditions might include, for example, lower temperatures or different reactant concentrations. In the case aqueous solutions, the addition of methanol, ethanol, or perhaps dimethyl carbonate would be required.



Thus, as shown, for a soluble base this approach might have the added benefit of regenerating the base for recycle, provided that an economical method of extracting the organic products could be devised. Unfortunately, the alkylation is not usually reported with methanol in the presence of soluble bases. Rather, a better alkylating agent such as CH_3Br is generally used. However, the alkylation reaction shown in the second step appears to be analogous to the O-alkylation of phenol with methanol over the CsNaX .

3.8.1 Reaction of Syringol in Aqueous NaOH: A series of experiments was performed in an attempt to quantify the reaction products of 2% syringol (2,6-dimethoxyphenol) in 1% aqueous NaOH (Na:Syringol = 1.9) as a function of time at 290 °C. The results are shown in Figures 24 and 25. As shown in the figures, the reaction products quantifiable by GC included methanol, guaiacol (2-methoxyphenol), catechol (1,2-hydroxybenzene) 2,3-dimethoxyphenol, 3-methoxycatechol, and 1,2,3-trimethoxybenzene. Very minor amounts of unidentified products were also detected by the GC.

In addition to the products shown in Figures 24 and 25, there must also have been a substantial fraction of products that were either not recovered from the reactor or that did not elute from the column. This is illustrated by the “ring balance” in Figure 24, which is simply a material balance on the aromatic rings. After 90 minutes of reaction time, about 75% of the aromatic rings initially present as syringol could not be accounted for in the reaction products. There are several possible rationalizations for this observation. First, the rings could have been gasified and therefore not recovered from the reactor. The KOH catalyzed gasification of pyrocatechol to H₂ and CO₂ has been reported to occur in supercritical water at temperatures > 500 °C [27]. Our reaction temperatures were much lower. In addition, aromatic compounds are expected to be more stable than methanol, one of the observed products. Further, there appeared to be no significant buildup of pressure in the reactor. Thus, we believe that a more likely explanation is that the rings reacted with one another to form higher molecular weight oligomeric or polymeric resins that were not eluted from the GC column. The reaction of phenolic compounds with formaldehyde (which could be formed from the product methanol) in the presence of alkali to form resins is well known, although the excess of methanol in the products (see below) does not seem consistent with this reaction occurring. To rule out the possibility that the products were not observed due to a lack of solubility, we tested a range of other solvents including ethyl ether, and toluene but no additional products were observed.

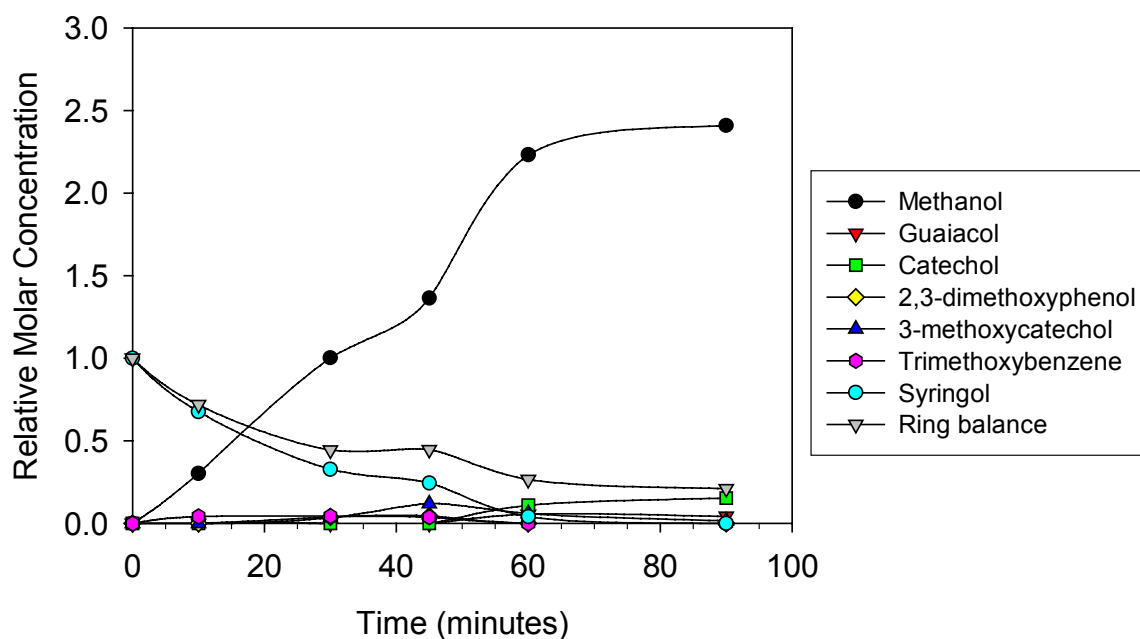


Figure 24. Reaction of syringol in aqueous NaOH at 290 °C (Na:syringol = 1.9) .

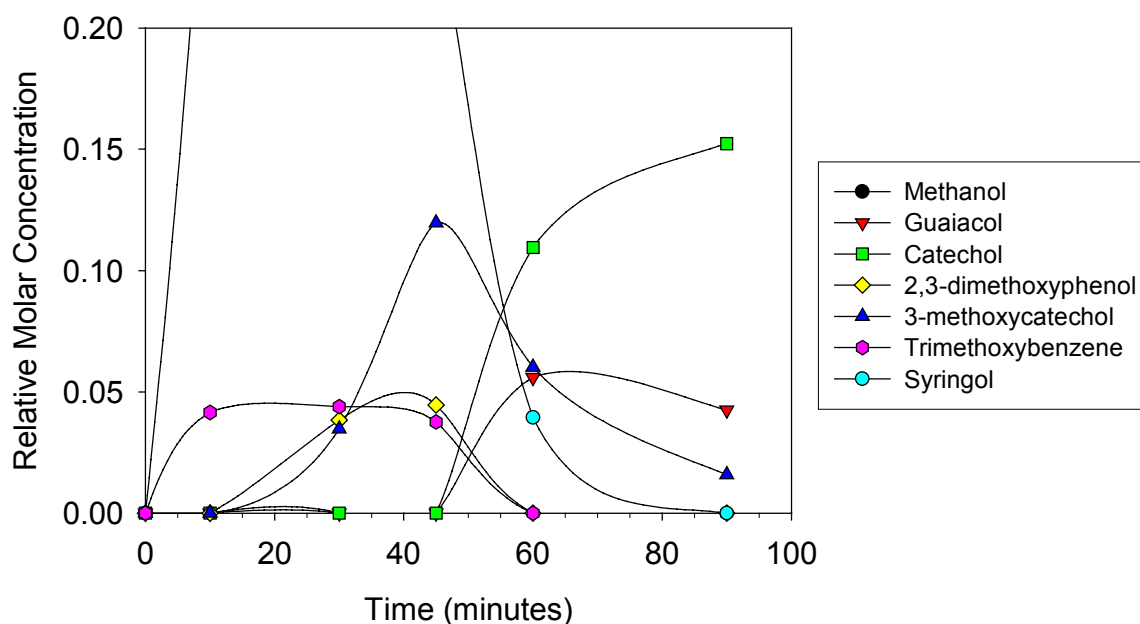
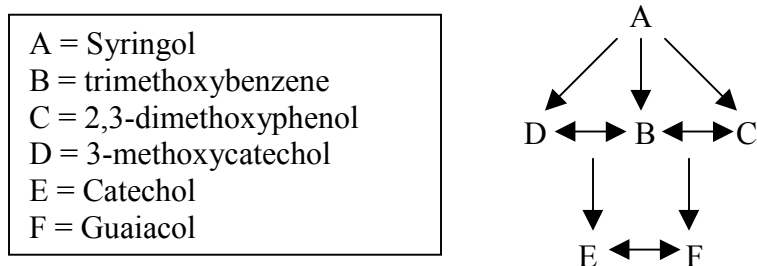


Figure 25. Detail of minor products from the reaction of syringol in aqueous NaOH at 290 °C (Na:syringol = 1.9).

Despite the lack of a good material balance on the aromatic rings, some insight into the reaction can be gained. From Figure 24 we can conclude that the reaction of syringol is relatively slow, only reaching completion after more than an hour. The exact reaction sequence is difficult to ascertain as a number of different pathways are available (see illustration below). Interestingly, at short reaction times, the syringol appears to react with itself to a small extent to produce trimethoxybenzene (Figure 25). Then, as the reaction progresses, the aromatic ring begins to be demethylated producing such compounds as 3-methoxycatechol, 2,3-dimethoxyphenol (in addition to being formed from the demethoxylation of trimethoxybenzene, this could also be formed through an internal migration of a methyl group), and guaiacol (demethoxylation). Eventually, as all the syringol is reacted, catechol becomes the predominant detectable aromatic compound. This sequence suggests that the migration or exchange of methyl groups between phenolic groups is kinetically favored, while demethylation and demethoxylation to form phenolic and other compounds is thermodynamically favored under our conditions.



As the methyl/methoxy groups are lost from the aromatic ring, they can be completely accounted for as methanol. Figure 24 shows that after 90 minutes there is actually about a 20% excess of methanol compared to the original methoxy groups (2 methoxy groups for every syringol molecule). It is possible that this excess methanol could account for some of the missing aromatic rings. However, it seems more likely that it is the result of errors in experimentation or quantification.

3.8.2 Reaction of Syringol and Phenol in Aqueous NaOH: A second series of model compound experiments involved reacting 2% syringol and 2.5% phenol in 1% NaOH (phenol:syringol = 2:1; Na:organics = 2:3) at 290 °C. The results are shown in Figures 26 and 27. A comparison of Figures 24 and 26 shows that the addition of phenol to the reaction mixture significantly changes the outcome. The most obvious differences are the appearance of anisole as a reaction product, and the absence of 2,3-dimethoxyphenol as a product. Also, the rate of syringol consumption is faster in the presence of phenol (5% remaining after 30 min) than without phenol (5% remaining after 60 min). Figure 26 also shows that the appearance of anisole mirrors the disappearance of phenol. Furthermore, the amount of methanol produced has been reduced by about the same amount of anisole that was formed (comparing Figures 24 and 26). Thus the data suggests that syringol reacts directly with phenol to produce anisole, much in the way methyl group exchange/migration appeared to occur between and within syringol molecules. Given the increased reaction rate and the absence of 2,3-dimethoxyphenol, the reaction between syringol and phenol appears to be favored over reactions of syringol with syringol. The increase in the reaction rate of syringol is consistent with the observation above that the methyl exchange reactions are kinetically favored.

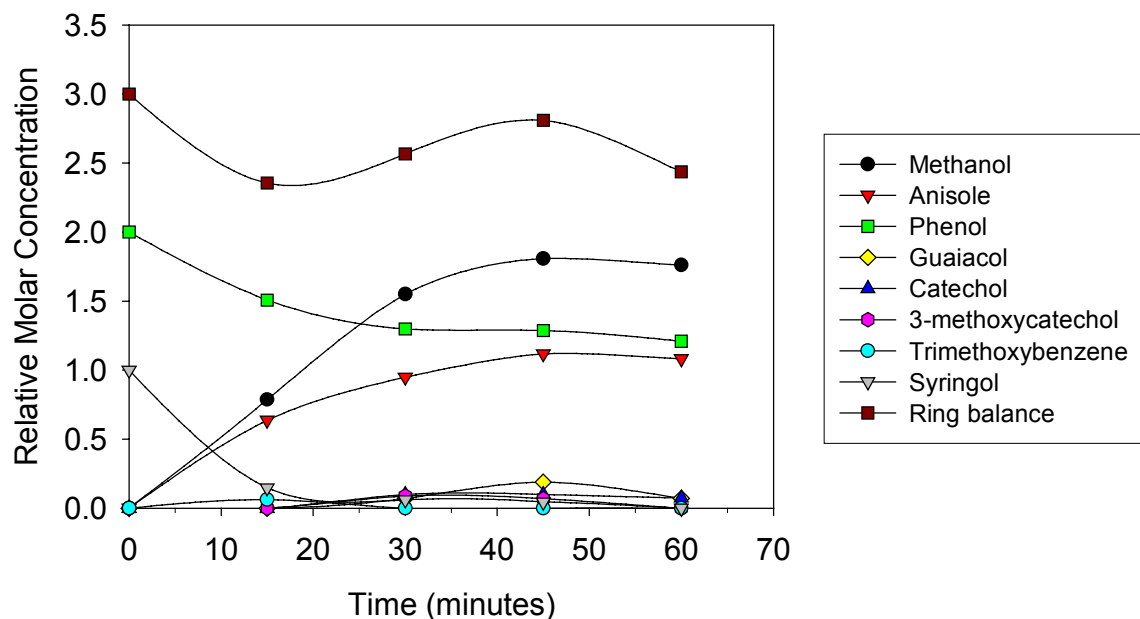


Figure 26. Reaction of syringol and phenol in aqueous NaOH at 290 °C (phenol:syringol = 2:1; Na:organics = 2:3).

As with the syringol experiments, the material balance on the aromatic rings shows a loss at long reaction times. Since the initial phenol can be accounted for as either phenol or anisole, this loss must again be associated with the syringol. As before, it appears that as much as 75% of the initial syringol can not be accounted for. Also as before, there appears to be an excess of methanol over what would be expected (accounting for the loss to anisole formation). Again, the reasons for this behavior are not known.

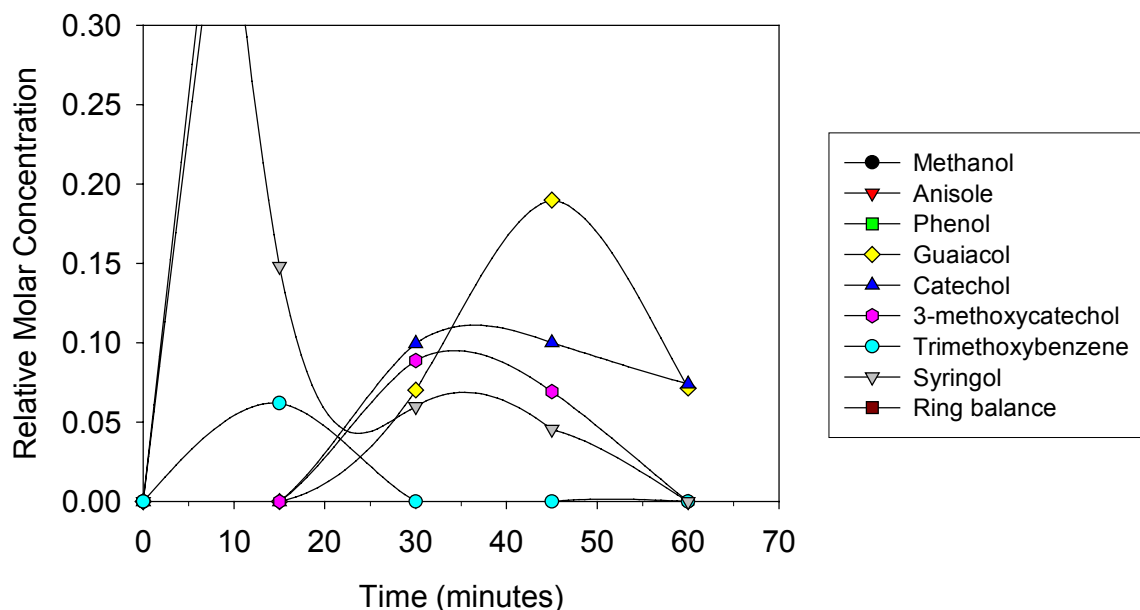


Figure 27. Detail of minor products from the reaction of syringol and phenol in aqueous NaOH at 290 °C (phenol:syringol = 2:1; Na:organics = 2:3).

An unexpected result was that anisole appears to be stable in the reaction mixture. That is, the concentration of anisole is virtually unchanged in extending the reaction time from 45 to 60 minutes (Figure 26). In the reaction of syringol alone, it appeared that methyl exchange reactions were kinetically favored, while a loss of methoxy functionality was thermodynamically favored. In addition, in a previous study, anisole was shown to be at least partly decomposed to phenol (and presumably methanol) by KOH in ethanol at 290 °C [13]. The apparent stability of anisole may be due to the neutralization of base by products from syringol decomposition, an equilibrium between phenol, methanol and anisole, or an inherent resistance to decomposition by aqueous base. This would be consistent with the results of Lee et. al. [25]. It is also possible that the result is an artifact, i.e. that anisole would react away at longer reaction times.

3.8.3 Reaction of Anisole in Aqueous NaOH: The unexpected production, and the apparent stability, of anisole in the reaction of syringol and phenol led us to perform a series of experiments to examine the decomposition of anisole by aqueous NaOH. The kinetics of anisole decomposition were determined by reacting 0.5g of anisole (0.0925 mol) in 3.7g 5% NaOH (0.0925 mol). The results are shown in Figure 28. Unlike reactions with syringol, the material balance was quite good for this reaction. This verifies that the material that could not be accounted for in the reaction of syringol and

anisole was associated with the syringol. The results also verify the expected stoichiometry of the reaction. In addition, the results demonstrate that after 1 hour of reaction time some of the anisole remains unreacted, and that the relative concentrations of the products are beginning to stabilize. This result is consistent with an equilibrium existing between anisole, phenol, and methanol.

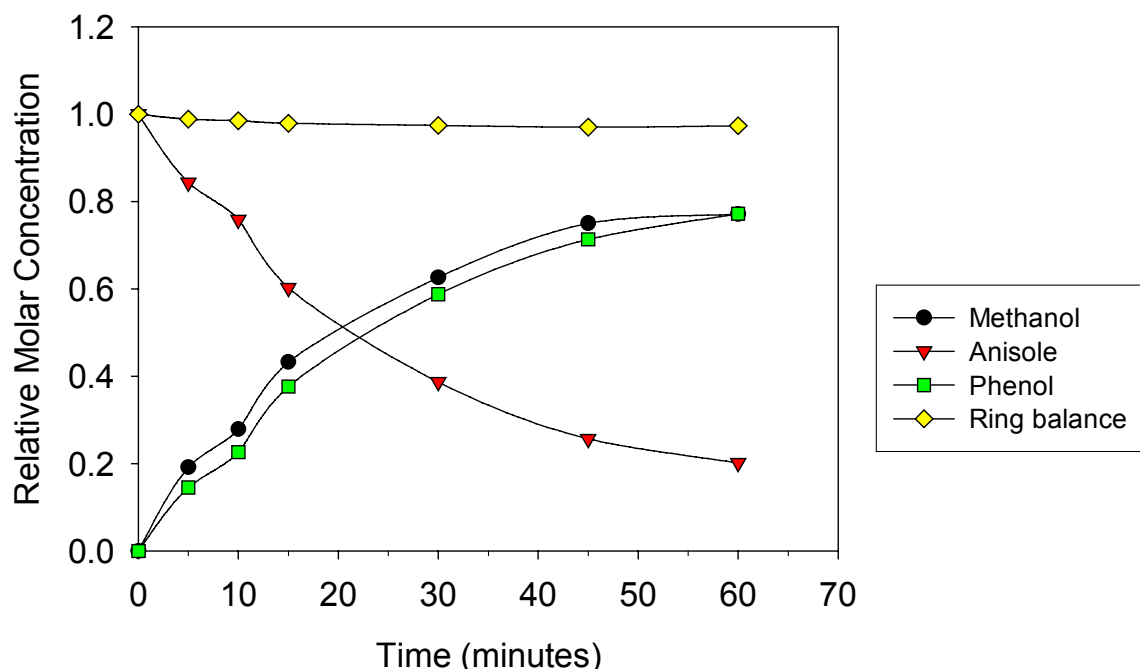


Figure 28. Reaction of anisole in aqueous NaOH at 290 °C (Na:anisole = 1:1).

Recall that we had also postulated that the stability of the anisole product from the reaction of syringol and phenol might be attributable to the neutralization of the NaOH by other reaction products. Thus we reacted anisole and NaOH for 1 hour at 290 °C using anisole:NaOH ratios of 1:2, 1:1, and 2:1. These tests showed that the relative concentration of anisole, methanol, and phenol in the products was not sensitive to the anisole:NaOH ratio. This result also suggests that the stability of anisole in the product mixture may result from an equilibrium between anisole, phenol, and methanol rather than base neutralization. However, we can not completely rule out base neutralization (from reactions of syringol) as a contributing factor.

3.8.4 Reaction of Phenol and Methanol in Aqueous NaOH: The results of the reaction of syringol with phenol as well as the reaction of anisole in aqueous NaOH suggest that there might be an equilibrium between phenol, anisole, and methanol at elevated temperatures in the presence of NaOH. To test this hypothesis, equal molar amounts of phenol, methanol, and NaOH were combined and allowed to react for 60 min at 290 °C. No anisole was observed in the products, apparently ruling out the postulated equilibrium. However, this appears to be in conflict with the results reported by Lee et. al. [25], particularly since our reaction conditions, aside from the catalyst, are not that far removed from theirs.

An alternate explanation that encompasses our results as well as those of Lee et. al. is that an equilibrium does exist for methanol, phenol, and anisole. However, aqueous NaOH does not offer a reaction pathway for methanol to react with phenol, while the zeolite does. Thus, in our case, once methanol is formed, it is kinetically trapped, and can not recombine with phenol. In other words, in the aqueous environment, methanol and phenol would be activated as methoxy and phenolate anions and would not react. The zeolite may offer other pathways, for instance activating the methanol as a methyl group that can then interact with the phenol much in the way that the methyl exchange/migration reactions occur. More detailed studies would be required to test this hypothesis.

3.8.5 Reaction of Methanol in Aqueous NaOH: Our studies with lignin showed a strong correlation between Na:lignin ratio and conversion, suggesting that base neutralization is a factor in limiting the overall conversion (Figure 16). In our earlier studies with alcohol solvents, we found that methanol and ethanol could be converted to carboxylic acids under the reaction conditions, thereby neutralizing the base catalyst [13]. Since our model compound studies indicated that methanol could be a significant product of lignin depolymerization, we performed a series of tests to determine if methanol could be reacting in aqueous NaOH to form formic acid, thereby neutralizing the base. The results, shown in Table 7, indicate that some neutralization of the NaOH does occur in the aqueous environment. Presumably the neutralization is due to the formation of formic acid from the methanol. However, even with a large (10:1) molar excess of methanol, the extent of neutralization is minor (< 15%). Therefore, it is unlikely that methanol formed during lignin depolymerization contributes significantly to the deactivation of the base catalyst.

Table 7. Reaction of methanol in aqueous NaOH at 290 °C for 60 min forms only small amounts of formic acid.

Methanol:NaOH	Time (min)	[OH]
10:1	0	0.2407
10:1	0	0.2436
10:1	0	0.2439
5:1	0	0.2326
1:2	60	0.227
10:1	60	0.2089
10:1	60	0.2062
10:1	60	0.2067

3.8.5 Conclusions from Model Compound Studies: Our model compound results are consistent with at least two different types of reactions occurring. Methyl migration/exchange reactions between phenolic groups (making and breaking ether bonds) appear to occur at relatively high rates. The loss of methyl and methoxy groups (destruction of ether linkages) to form methanol is a slower process, but is evidently favored at long reaction times. This could mean that the loss of methyl groups to methanol formation is thermodynamically favored. However, kinetic trapping of the

methyl groups in the form of methanol appears to offer a better rationalization of our data with that found in the literature.

The more highly substituted compounds (syringol) appear to be less stable than compounds with lesser substitution (anisole). As expected, the product spectrum from the decomposition of syringol is more complex than that arising from the decomposition of the simpler compound anisole. Unfortunately, the poor material balance on aromatic rings suggests that a large fraction of the syringol may undergo retrogressive (polymerization) reactions or gasification. Additional studies would be required to determine if these unidentified types of products are capable of neutralizing NaOH. The reason that syringol reacts in this way, is not well understood. However, based on the limited evidence at hand, we speculate that the unaccounted-for products result from reactions in which the oxygen linkage is cleaved from the aromatic ring. To elaborate, in the case of syringol, products such as catechol and guaiacol demonstrate that linkages between the aromatic ring and oxygen can be broken. In contrast, the reaction of anisole produces only phenol and methanol; no benzene is produced, and virtually all the aromatic rings are accounted for in the material balance.

Methanol appears to be the principal product from the demethylation/demethoxylation reactions in all cases. Although methanol does appear to react further to produce formic acid, the rate of this reaction is slow enough that it is unlikely to significantly contribute to the neutralization of the base catalyst.

4. Summary and Conclusions

High conversions of lignin to water and ether solubles are possible by depolymerization with aqueous NaOH. When an excess of NaOH was used relative to lignin monomers, only 8% insoluble material remained after treatment at 330 °C for one hour, and only 15% insoluble material remained after a one hour treatment at 290 °C. Although direct comparisons are difficult, it appears that the kinetics of lignin conversion, although reasonable, are somewhat slower with aqueous NaOH than with KOH in alcohol (compare to data in [13]). With a large molar excess of NaOH (10% NaOH, Na:lignin = 4.6) the insolubles reach a minimum within the first 25 minutes at 290 °C. The reaction kinetics are slower for less concentrated solutions. The addition of CaO (or Ca(OH)₂) to the reactor increases the rate of the depolymerization reaction, but does improve the ultimate degree of lignin conversion.

The means by which CaO improves the reaction kinetics is not well understood, but it appears to be related to changes in the pH of the reaction mixture. Mixtures that contain both CaO and NaOH resist neutralization by reaction products. Our results suggest that the reaction products responsible for neutralizing the base are weak organic acids. In contrast, David Johnson at NREL has directly observed CO₂ formation in quantities large enough to account for the neutralization. In our case, CaO should be an effective scavenger for CO₂ formed during the reaction. Therefore, it is likely that both CO₂ and weak organic acids are capable of contributing to the neutralization process.

Since CaO increases the rate of conversion, but not the extent of conversion, we postulate that lignin conversion depends on both the OH^- and Na^+ concentrations. CaO is able to provide OH^- ions (as evidenced by the high pH after reaction). It appears, though, that it is unable to prevent the consumption of Na^+ ions. Thus, the rate remains higher than it would if both OH^- and Na^+ were being consumed, but ultimately falls to zero when all the Na^+ is consumed by the depolymerized lignin.

For long reaction times, the primary factor governing the extent of lignin conversion is the NaOH:lignin ratio. NaOH concentration (i.e. water:lignin ratio), per se, is at best a secondary issue. There may be a positive effect at very high water:lignin ratios (beginning at about 0.5% NaOH). However, as the dilution increases, the cost of constructing and operating a reactor increases. The maximum lignin conversion is achieved at NaOH:lignin mole ratios of 1.5 – 2 (assuming a molecular weight for lignin monomers of 180). Higher ratios do not lead to further increases in conversion. If lower ratios are used, some benefit can be obtained by recycling the unconverted lignin. However, less lignin overall would be converted than if the NaOH:lignin ratio were carefully controlled during the first pass.

The combination of Na_2CO_3 and CaO offers a cost saving alternative that performs identically to NaOH on a per Na basis (the reaction of Na_2CO_3 and CaO forms NaOH and CaCO_3). A quick review of bulk chemical prices suggests that the price of NaOH is 2-3 times higher than the price of the Na_2CO_3 / CaO combination on a Na atom basis. We have proposed a base recovery and recycle process wherein the precipitated CaCO_3 is recovered and converted back to CaO through calcination, and the Na is recovered as Na_2CO_3 or NaHCO_3 by neutralization of the product solution with pressurized CO_2 . Additional work is required to determine if the recovery and recycle process is feasible and provides additional cost savings.

Our model compound studies reveal that, under reaction conditions, the migration of methyl groups between phenolic groups (making and breaking ether bonds) occurs at a relatively high rate. The loss of methyl and methoxy groups from the aromatic ring (destruction of ether linkages) is a slower process, but is favored at long reaction times. This trend appears to be better rationalized by a model in which methyl groups are kinetically trapped in the form of methanol, rather one in which the reaction is driven by a thermodynamic equilibrium. The more highly substituted compounds (syringol) are more reactive than compounds with lesser substitution (anisole), and give rise to more products. The results suggest that the more complex molecules may undergo retrogressive reactions to higher molecular weight products. However, our results do not rule out the possibility that the complex molecules are gasified, e.g. to CO_2 and H_2 . This additional reactivity may be related to reactions in which the oxygen linkage is cleaved from the aromatic ring. Methanol is the principal product from the demethylation and demethoxylation reactions. Once formed, methanol appears to react further to produce formic acid, but at a rate that is too slow to significantly contribute to the neutralization of the base catalyst.

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